STRUCTURAL AND THERMAL STUDIES OF MAGNESIUM TARTRATE CRYSTALS GROWN BY GEL TECHNIQUE

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ABSTRACT

Tartrate crystals have wide applications. So, their growth procedure and their characteristics are very significant for industrial development. For the applications, the grown crystals have to be characterized and evaluated for their properties and behaviour. Single crystals of magnesium tartrate tetrahydrate were grown by single diffusion silica gel technique at ambient temperature. The obtained crystals were opaque having dimensions of 3 X 2 X 2 mm^3. The powder XRD analysis showed these crystals to have orthorhombic crystal system. The lattice parameters are found to be; a = 9.1820 Å, b= 11.2062 Å and c = 7.9529 Å. *FTIR spectral analysis confirmed the presence of water of crystallization and various related groups and bonds. The presence of expected elements in crystals was confirmed by carrying out EDAX spectrum analysis. UV-Vis-NIR spectral study reveals these crystals to be transparent and suitable for second harmonic generations.* The obtained band gap energy value in the present study is found to be 4.776 eV. *The scanned images show these crystals to be grown by layer deposition. Thermogravimetric analysis (TGA) confirms the presence of water molecules in the lattices and reveals the decomposition behavior of the crystals in the temperature range of 30-800 ^oC. Experimental data of TGA are used to generate the chemical formula for grown MT crystals. MT crystals are found to possess a chemical formula: $MgC_4H_4O_6.4H_2O$ with a molecular weight of 244.403. The thermal stability of the crystals was found to be 39 ^oC. By using the standard Broido relation, the activation energy and various kinetic parameters such as change in entropy, change in enthalpy and Gibbs free energy for all the crystals were obtained and studied.*

Keyword: - *Gel growth, PXRD, EDAX, UV-Vis-NIR, FTIR, SEM ,TGA*

1. INTRODUCTION

Tartrate single crystals have many interesting and useful properties such as ferroelectric, piezoelectric, dielectric, optical and other technological characteristics [1-8]. The powder XRD and FTIR studies were made on the gel grown Magnesium Tartrate crystals and reported by Dave M.P. et al [9]. In present work, single crystals of Magnesium tartrate crystals were synthesized by silica gel technique and the grown crystals were characterized by carrying out various structural analyses such as powder XRD, EDAX spectral, UV-Vis-NIR spectral, FTIR spectral and SEM.

2. EXPERIMENTAL DETAILS

2.1 Crystal growth

Single crystals of magnesium tartrate crystals were grown by using the silica gel as a growth medium. The chemical used for the growth were tartaric acid, magnesium chloride and sodium metasilicate. All chemicals were AR grade. The crystallization apparatus consists of borosilicate glass test tubes having dimensions of 20 cm x 1.5 cm were placed vertically on a wooden stand. The solutions of tartaric acid and magnesium chloride were prepared by dissolving these compounds in an appropriate amount of distilled water. The solutions were stirred and filtered using filter paper. The solution of sodium metasilicate was prepared by adding its compound in to distilled water in appropriate amount. It was stirred and kept for a day so that all the impurities settle down. Then the solution is filtered and kept aside. To get the required specific gravity of gel, the calculated amount of distilled water is added into sodium metasilicate solution. Silica gel is prepared by acidifying sodium metasilicate solution with tartaric acid drop by drop with continuous stirring to avoid excessive local ion concentration which may cause premature local gelling and make the final solution inhomogeneous and turbid. The pH of the gel was adjusted to attain the value of

4.5. The gelling mixture was transferred in to test tubes and allowed to set by keeping undisturbed. The open end of the test tubes was closed using cotton plug to prevent excess evaporation and contamination from the exposed surface of the gel. Here, the tartaric acid acted as lower reactant. After confirming the gel setting, an aqueous solution of Magnesium Tartrate was carefully poured along the walls of the test tube with the help of pipette over the set gel in order to avoid any gel breakage.

The following reaction is expected to take place in the gel medium.

$$MgCl_2 + C_4H_6O_6 \rightarrow MgC_4H_4O_6 + 2HCl \quad \text{…….....} \quad (1)$$

2.2 Characterization techniques

The grown Magnesium tartrate (MT) crystals were subjected to the powder crystal XRD studies using Rigaku Miniflex X-ray Diffractometer with CuKα radiation (λ=1.54 Å). The sample was scanned over a required range for 2Θ values (0-80̊). The elemental analysis was carried out by using EDAX spectral analysis. The FTIR spectra were recorded for the powdered sample in the range 400-4000 cm^{-1} using Perkin Elmer (Model: Spectrum BXw) spectrophotometer by using KBr pallet technique. The UV-Vis-NIR absorption spectra were recorded for all the three grown crystals using Shimadzu UV-1700 spectrophotometer in the wavelength range of 200-1100 nm. Surface morphology of grown crystals was studied by using Hitachi S-3400N scanning electron microscope.

3. RESULT AND DISCUSSION

3.1 Crystal growth

The crystals were harvested after 42 days. They were washed and cleaned by using distilled water. The crystals were opaque having the size of 3x2x2 mm^3. The growth condition is shown in table -1. The grown MT crystals are shown in figures 1(a) and 1(b).

Table - 1: Growth conditions

Sp. density of Sodium meta silicate	1.048 gm/cc
Concentration of Tartaric acid	0.5 M
pH of the silica gel	4.5
Concentration of Magnesium Chloride	0.5 M
Gel setting period	5 days
Gel aging period	2 days
Period of crystal growth	42 days
Temperature	Ambient Temperature

Fig-1(a): Growth of MT crystals

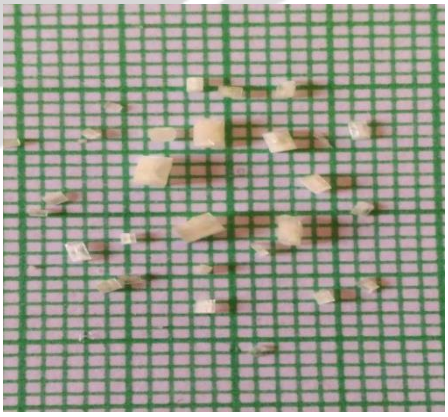

Fig-1(b): Grown MT crystals

3.2 Powder XRD analysis

From the obtained XRD data, the observed prominent peaks confirm the crystalline nature of the grown MT crystals. The d values of crystals matched well with those of reported data [9]. The d values correspond to the orthorhombic crystal system. From the reported data the lattice parameters are found to be; a = 9.1820 Å, b= 11.2062 Å and c = 7.9529 Å. The hkl values were obtained using lattice parameters by using the formula;

$$1/d^2 = (h^2/a^2) + (k^2/b^2) + (l^2/c^2) \quad \text{.....(2)}$$

The XRD spectra for both the crystals are shown in figure 2. The relative intensities and (hkl) of MT crystals are tabulated in table - 2.

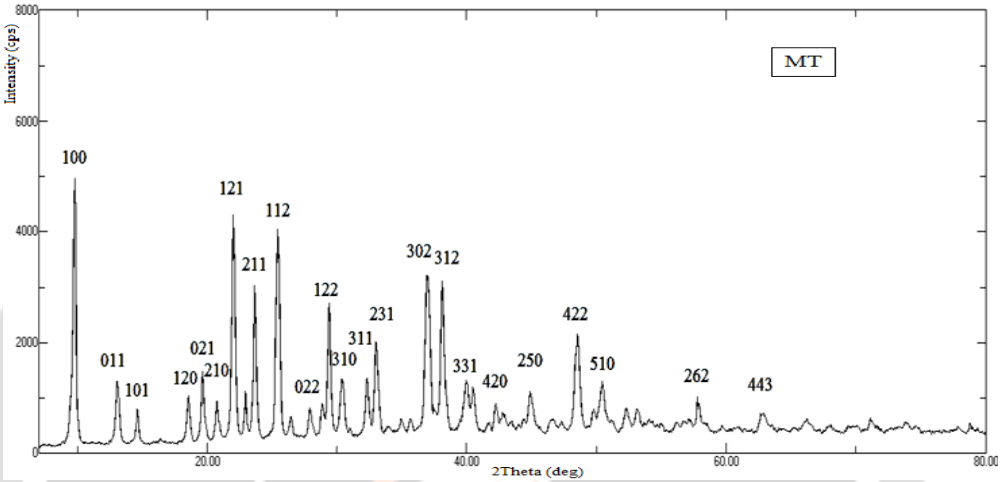

Fig -2: XRD Spectra of MT crystal

Table - 2: Relative intensities, 2Θ degrees, d values and hkl planes of MT crystals

Relative intensity I/I_0	2Θ degrees (observed)	d(Å) (observed)	d(Å) (calculated)	(hkl)
100	9.82	9.00	9.18	100
24	13.04	6.78	6.49	011
14	14.62	6.05	6.01	101
18	18.56	4.78	4.78	120
27	19.64	4.52	4.58	021
15	20.74	4.28	4.25	210
85	22.02	4.03	4.10	121
58	23.66	3.76	3.75	211
79	25.44	3.50	3.47	112
10	27.86	3.20	3.24	022
50	29.40	3.04	3.06	122

3.3 Elemental analysis

The spectra obtained from Energy Dispersive X-ray analysis confirm the presence of various elements in the grown crystals as shown in figure 3. The presence of Magnesium in pure MT crystal is confirmed. In the Magnesium tartrate crystal sample, the peak ranging from 1.1 KeV to 1.3 KeV clearly indicates the presence of Magnesium. The relative weight is 21.95 %, while the relative atomic weight is 14.67 %. Obtained EDAX data are shown in table - 3.

Table - 3 : EDAX data of Magnesium Tartrate

Element	Observed W%	Observed A%
C	18.12	24.50
O	59.94	60.84
Mg	21.95	14.67

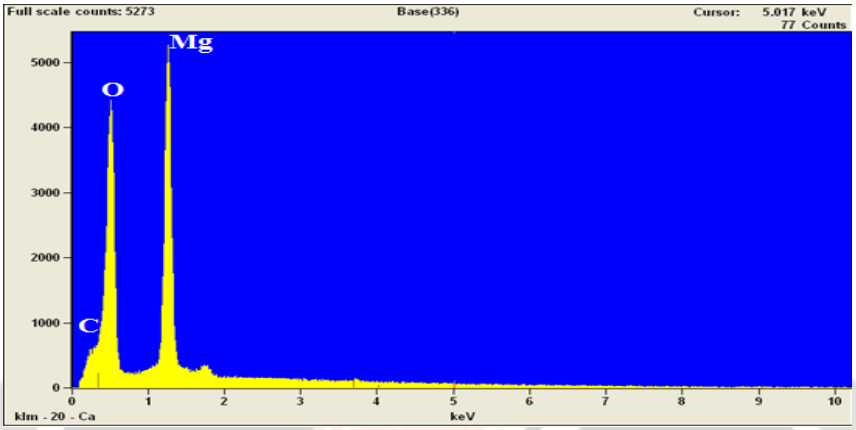

Fig- 3 : EDAX graph of Magnesium Tartrate

3.4 FTIR spectral analysis

The observed absorption bands/peaks and their respective assignments for Magnesium tartrate crystals are reported in table 4. The assignments for the absorption bands/peaks of FTIR spectrum of the grown pure MT crystals in the present study are in good match with the previously reported data [9]. The obtained FTIR spectrum can be seen in figure 4.

Table-4: IR assignments for MST crystals

Wave numbers in cm^{-1}	Peak assignments
3432, 2830,2729	Water, OH stretch & C-H stretch
2360	Combination and overtone bands
1610	C=O stretch
1389	C-OH in-plane bend
1329	In-plane and out of C-H bend
1127	O-H deformation out of plane
1065	C-O(H) stretch
933	C-C stretch
720	Metal-Oxygen bonding

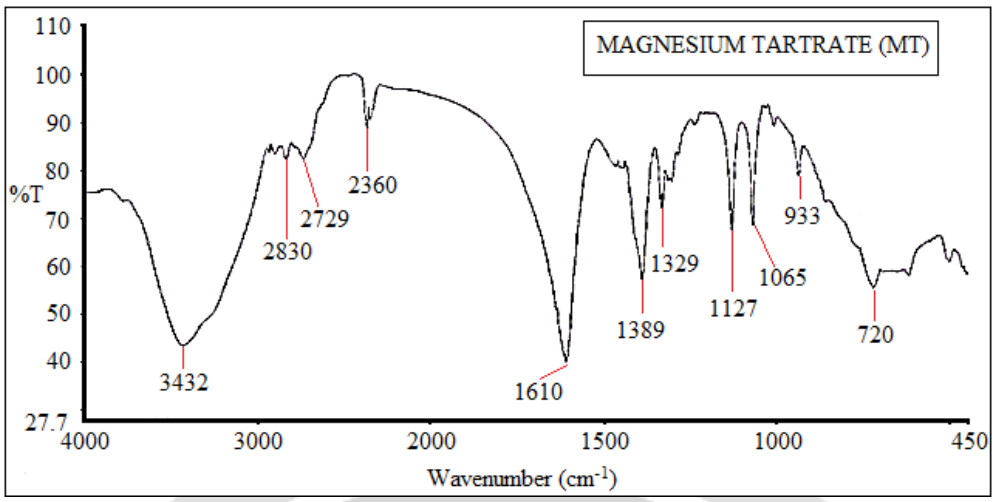

Fig-4 : FTIR spectra of MST

3.5 UV-Vis-NIR spectral analysis

The UV-Vis absorption patterns obtained are shown in figure 5. The spectrum shows wide transmission window in the visible region which enables it to be potential candidate for opto-electronic application. The presence of low cut off wavelength and the wide optical transmission window range are the most desirous properties of materials possessing NLO activity. The low absorption in the visible region confirms the suitability of the grown crystals for NLO applications.

From the lower cut off wavelength, band gap energy was calculated using the formula:

$$E = h\nu = hc/\lambda \quad \text{..... (3)}$$

Where, $h = 6.623 \times 10^{-23}$ Js, $c = 3 \times 10^{8}$ ms^{-1}.

The observed cut off wavelength and the obtained band gap energy value in the present study is provided in table 5.

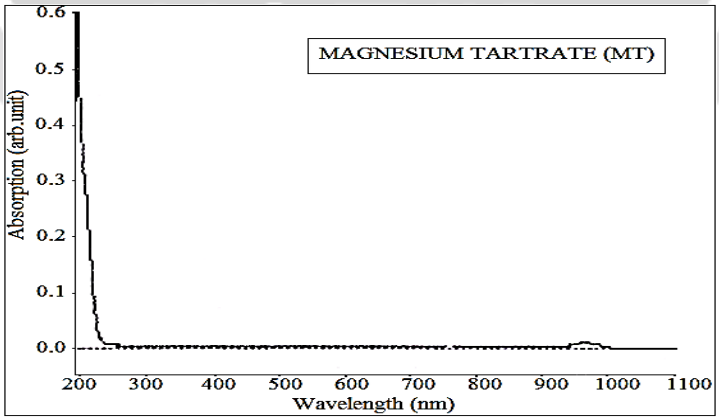

Fig-5: UV-Vis spectrum for MT

Table-5: Band-gap energies of MST crystals

Sample	Cut-off wavelength λ (nm)	Band-gap Energy E (eV)
MT	260	4.776

3.6 Structural analysis

Figure 6(a), (b), (c) and (d) are scanned images of pure magnesium tartrate (MT) crystal. In Figure 6(a), the growth layers can be seen very clearly on the crystal surface. Figure 6(b) shows magnified image of scanned crystal. Here, plate like and rod like tiny crystal particles attached on the surface of crystal can be seen. In figures 6(c) and 6(d) thick and thin growth layers are seen on the crystal surface, indicating that the growth was happened by layer deposition technique.

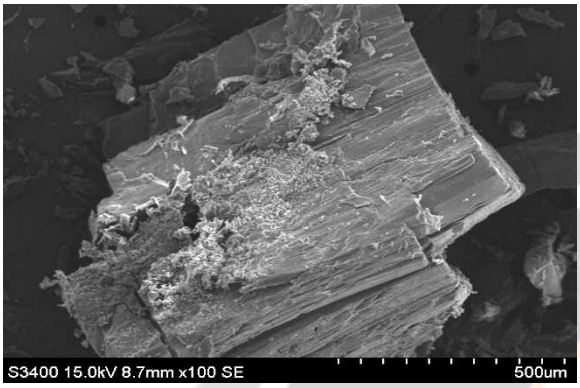

Fig-6 (a): Scanned image of MT crystal

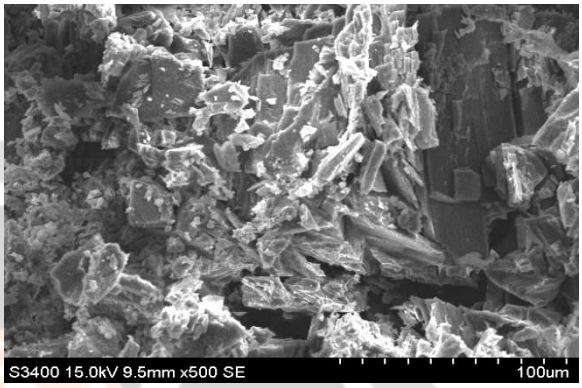

Fig-6 (b): Scanned image of powdered MT

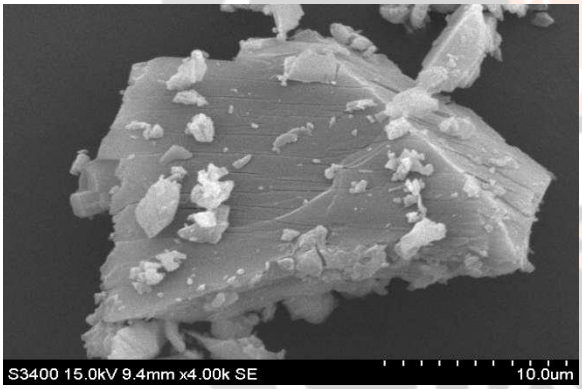

Fig-6 (c): Growth layer on the surface of MT

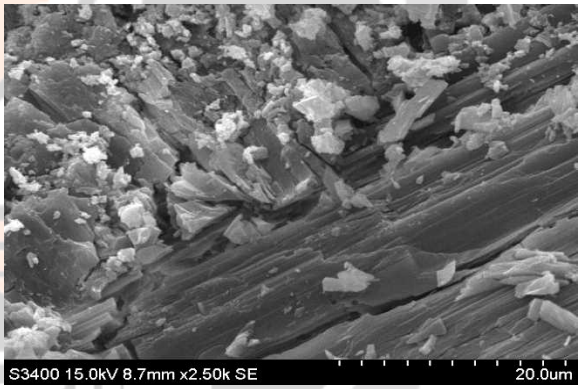

Fig-6(d): High magnified image of powdered MT

3.7 Thermal analysis

In the present work, the thermo gravimetric analysis of grown crystals were carried out at a constant heating rate of 10 ˚C min^{-1} in the temperature range from ambient to 800 ˚C by using Perkin Elmer Thermo Gravimetric Analyzer (Model name: Pyris-6 TGA).

3.7.1 Thermal behavior

The thermal decomposition behaviors of the grown crystals were studied using the obtained thermogram. as shown in figure 7. The initial weight taken for thermogravimetric analysis was 10.318 mg. Here the decomposition starts at 39℃. This indicates that the pure MT crystal is stable up to 39℃. The first stage of decomposition between 39℃ to 197℃ indicates formation of magnesium tartrate tertrahydrate to magnesium tartrate anhydrate. Here four water molecules are dehydrated in first stage. From this TG analysis, we can confirm that the crystal sample is tetrahydrate, as it contains four water molecules. The second stage of decomposition starts at 260℃ and is completed at 413℃ resulting in the formation of magnesium oxalate, which remains stable up to 431℃. In the third stage between 432℃ and 616℃, magnesium oxalate decomposes to magnesium carbonate. The summery of the

decomposition steps, the expected and observed mass loss and loss of molecules at different stages are provided in table 6.

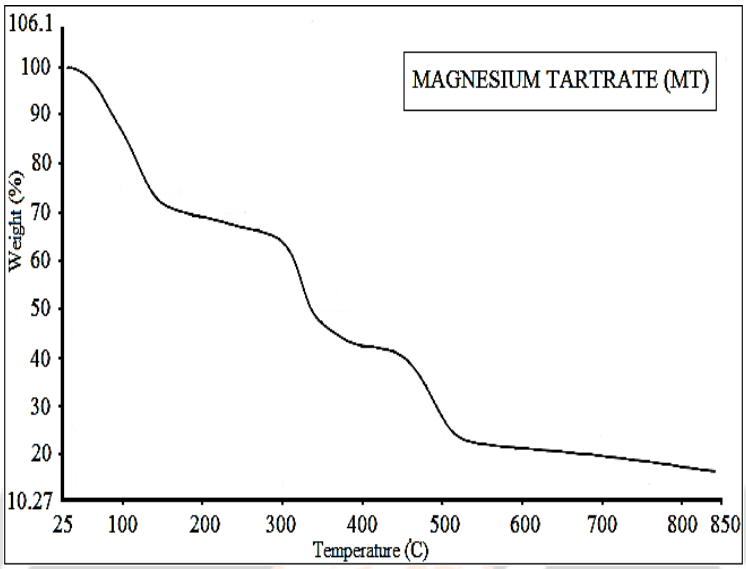

Fig-7: Thermogram of MT crystal

Table-6: Weight loss in different stages of decomposition of MT crystals

Sample	Stage	Temperature range (℃)	Weight loss (%)		Loss of molecules
			Observed	Calculated	
MT	1	39 - 197	30.489	29.48	$4H_2O$
	2	260 – 413	24.438	24.56	$2C$ & $2H_2O$
	3	432 – 616	20.430	11.45	CO

3.7.2 Kinetic study

In the present work, the method of Broido [10] has been employed for the estimation of energy of activation for thermal degradation. TGA graphs are taken in a definite temperature range (30 °C to 800 °C).

Broido Relation

Broido [11] has suggested a simple and sensitive graphical method of treating TGA data when a crystal is heated and undergoes pyrolysis. It is assumed that the pyrolyzed products are volatile. The progress of the reaction can be determined by continuous weighing of the sample. According to this method, the weight of the material W_t at any time is related to the fraction of the number of initial molecules not yet decomposed N/N_0 by the equation:

$$Y = N/N_0 = (W_t - W_\infty) / (W_0 - W_\infty) \text{ ……...(4)}$$

Where, W_0 = initial weight of the sample,
W_∞= weight of the residue at the end of the degradation,
W_t = weight of active material at an absolute temperature T.

Integrating and taking logarithms, one contains,

$$\ln \ln (1/Y) = E/RT + \text{Constant……..(5)}$$

Activation energy, $E = \text{slope x } R$ ……..…..(6)

Entropy is a thermodynamic quantity representing the amount of energy in a system that is no longer available for doing mechanical work. The change in entropy is given by,

$$\Delta S = 2.303\ R \log (Ah/KT) \ldots\ldots\ldots\ldots (7)$$

Where, A = Frequency Factor,
K = Boltzmann's Constant,
T = Average Temperature,
R = Gas Constant.
h = Plank's Constant

Enthalpy is a thermodynamic quantity equal to the internal energy of the system plus the product of its volume and pressure. The change in enthalpy is given by,

$$\Delta H = E - 2RT \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

Where, E=Activation energy.

Gibb's free energy is given by,

$$\Delta G = \Delta H - T\,\Delta S \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (9)$$

The obtained activation energy, change in entropy, change in enthalpy and change in Gibb's free energy values are tabulated in table 7.

Table-7: Activation energy and Thermodynamic parameters for MT crystal

Samples & Stages		Activation Energy E (eV/mol)	Frequency Factor A (S^{-1})	Change in Entropy ΔS (eV/K.mol)	Change in Enthalpy ΔH (eV/mol)	Gibb's Free Energy ΔG (eV/mol)
MT	1	2.57×10^{23}	2.22×10^{5}	9.06×10^{20}	2.16×10^{23}	5.76×10^{23}
	2	8.23×10^{23}	1.14×10^{11}	2.45×10^{20}	7.59×10^{23}	9.09×10^{23}
	3	8.32×10^{23}	5.99×10^{8}	5.32×10^{20}	7.48×10^{23}	1.17×10^{24}

We can see that the activation energies E are increased in all three stages, indicating that more energy is required to start the decomposition in each stage. The change in entropy ΔS is negative for all three stages, indicating that the disorder of the system has decreased. Here, the value of ΔH is positive for all three stages, indicates that the reaction is endothermic. That means the heat is absorbed by the system due to the products of the reaction having a greater enthalpy than the reactants. Here, ΔG is positive for all decomposition stages. This indicates that the reaction is endergonic reaction, which means that the system is absorbing energy in the form of work.

4. CONCLUSION

Pure Magnesium tartrate crystals have been grown in silica gel at ambient temperature. The obtained crystals were opaque having dimension of 3X2X2 mm^3. From PXRD spectrum, the sharp peaks declare the perfect crystalline nature of crystals. These crystals were found to have orthorhombic crystal system. From EDAX spectra, the presence of all the expected elements was confirmed. From FTIR spectral analysis the presence of water of crystallization and related groups and bonds were confirmed. It is inferred from the UV-Vis-NIR spectrum that the crystals have low absorbance in the entire visible & NIR regions and show maximum absorption at UV region. From these it can be considered as promising nonlinear optical (NLO) crystals. The scanned images show these crystals to be grown by layer deposition. From thermal analysis of MT crystals, we found that the thermal stability of pure MT is 39 ^{o}C. Also, these tartrate crystals lose four water molecules in first decomposition stage. This indicates that the Magnesium tartrate crystals have four water molecules, i.e. they are tetrahydrate crystals. Activation energy of first stage decomposition is comparatively lesser than that of other stages, which indicates that lesser activation energy is required for water molecule to release from crystals.

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