

Growth of Racemic Tartaric Acid Single Crystal and Characterization

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Abstract: Single crystal of Tartaric acid monohydrate, a racemic tartaric acid, has been grown by slow solvent evaporation technique. The maximum size of the crystal obtained is 34x25x15 mm³. The grown crystals were subjected to various characterizations in order to reveal its properties. Single crystal X-ray diffraction studies were carried out in order to confirm the compound, and the obtained cell parameters were compared with the literature values. Moreover the compound was confirmed by the identification of functional groups using Fourier transform infrared analysis. The grown crystal was subjected to optical studies to find the transmittance in the ultraviolet, visible and infrared radiation of wavelength in the range 200 to 1100 nm. Thermal studies such as Thermogravimetric and Differential thermal analysis were carried out to find the thermal stability of the grown crystal. Vicker's microhardness testing was made on the as grown crystalline surface to find the surface hardness, yield strength and other related mechanical properties of the crystal.

Keywords: Crystal growth; Crystal structure; X-ray diffraction; Organic compounds; Thermogravimetric analysis

1. Introduction

Tartaric acid is an important carboxylic acid in organic compounds, which is also called as dihydroxy butanedioic acid. It is a chiral molecule, which exists as three stereoisomers: D-tartaric acid, L-tartaric acid and meso-tartaric acid. These molecules have slightly different structures and racemic tartaric acid is an equal mixture of two enantiomers D-tartaric acid and L-tartaric acid compounds. Tartaric acid is an optically active compound. It can form salts with bases, and some of the important salts of tartaric acid are cream of tartar (potassium hydrogen tartrate) and Rochelle salt (potassium sodium tartrate). A chiral molecule is not necessarily asymmetric, that is, devoid of any symmetry elements. A mixture of equal amounts of the two enantiomers is said to be a racemic mixture. Racemic mixtures are not optically active even though their two enantiomer constituents are separated. L-Tartaric acid combine with amino acids and bases to produce nonlinear optical crystalline compound [1-5] and it helps to influence the nonlinear effect by combine with KDP [6]. In view of finding new nonlinear optical crystal, research was undertaken and revealed the properties of racemic tartaric acid. In this article, we are presenting the growth, spectroscopic, optical, mechanical and thermal characteristics in this article.

2. Crystal Growth

The title compound Tartaric acid monohydrate was grown by slow solvent evaporation technique with distilled water as solvent. A homogeneous aqueous solution of tartaric acid monohydrate was prepared by stirring 4 hours continuously using magnetic stirrer. The optimum pH value of the solution was measured as 4. Then the prepared solution was made to

evaporate slowly at room temperature in a dark room. After 20-30 days, good optically transparent single crystals of various sizes were harvested from the mother solution. The photograph of the as grown crystal is shown in the Fig.1. The maximum size of the crystal obtained is 34x25x15 mm³.

3. Experimental Methods

In order to reveal the properties of the crystal, the grown tartaric acid monohydrate single crystals were subjected to different characterization. The crystal structure and space group were analyzed and confirmed by single crystal X-ray diffraction, which was carried out using a Bruker AXS Kappa APEX II single crystal CCD diffractometer coupled with graphite-monochromated MoK α ($\lambda=0.7107\text{\AA}$) radiation.





Figure 1: Photograph of Tartaric acid monohydrate crystal a) before and b) after recrystallization

The goniometer equipped with the diffractometer is four circle goniometer with φ , χ , ω and 2θ axes by which the crystal is rotated. The crystal of size $0.30 \times 0.20 \times 0.20 \text{ mm}^3$ was cut and mounted on a glass fiber using cyanoacrylate. The structure was solved by direct method with the aid of SHELXS97 (Sheldrick, 2008) and refined using SHELXL97 (Sheldrick, 2008) by the methods of full-matrix least squares refinement. Carboxylic group (-COOH) is the easiest functional group to detect by infrared spectroscopy, since this group can be considered as being formed from C=O and O-H units. In order to identify the functional groups present in the grown crystalline compound, Fourier Transform Infrared (FTIR) spectroscopic analysis was carried out between 4000 and 400 cm^{-1} using Perkin-Elmer spectrum one FTIR spectrometer. A good optical material should possess high transmittance in the visible region and hence in this point of view, UV-Vis-NIR transmission spectrum of tartaric acid monohydrate single crystal was studied in the range of 200 to 1100 nm using Perkin Elmer Lambda 35 UV/VIS spectrometer to determine its transmittance and hence to know the suitability of tartaric acid monohydrate single crystal for any optical device. The crystal of 3 mm thickness was used for recording the spectrum.

Microhardness plays an important role in any device fabrication. In order to find the surface hardness of the grown tartaric acid monohydrate single crystal, Vicker's microhardness studies were carried out using Reichert-Jung MICRO-DUROMAT 4000 E microhardness tester. The basic principle, as with all common measures of hardness, is to observe the questioned material's ability to resist plastic deformation from a standard source. It was carried out on the on growing crystal plane using microhardness tester provided with a Vicker's diamond pyramidal indenter. The hardness values were calculated from the formula $H_v = 1.8544 P/d^2 \text{ kg/mm}^2$, where P is the applied load, d is the mean diagonal length of the indentation and 1.8544 is a constant of a geometrical factor for the diamond pyramid. The sample was subjected to load ranging from 5 g to 100 g by a diamond indenter and the measurements of indentation size were performed using the optical system of that apparatus. A set of two indentations were measured for each load level by the same operator. In order to find phase change, decomposition and melting point of the grown tartaric acid monohydrate

single crystal, Thermogravimetric analysis (TGA), Differential thermal analysis (DTA) and Differential scanning calorimetric (DSC) studies were carried out between the temperature $25 \text{ }^\circ\text{C}$ and $500 \text{ }^\circ\text{C}$ in nitrogen atmosphere at a heating rate of $10 \text{ }^\circ\text{C/min}$ using NETZSCH STA 409 TG/DTA instrument.

4. Results and Discussions

Tartaric acid monohydrate crystal was confirmed that it crystallizes triclinic structure with the centrosymmetric space group of $P\bar{1}$ from the X-ray diffraction analysis. The unit cell parameters obtained are $a = 4.889 \text{ \AA}$, $b = 8.052 \text{ \AA}$, $c = 9.181 \text{ \AA}$, $\alpha = 109.180^\circ$, $\beta = 99.98^\circ$, $\gamma = 96.05^\circ$ and volume $V = 331 \text{ \AA}^3$. When they are compared with the reported values, the result is highly agreed with them [7]. It is confirmed as a racemic tartaric acid, which is a mixture of D-Tartaric and L-Tartaric acids in equal proportion of weight. The Fourier transform infrared spectrum for the Tartaric acid monohydrate compound is shown in the Fig.2. In this spectrum the

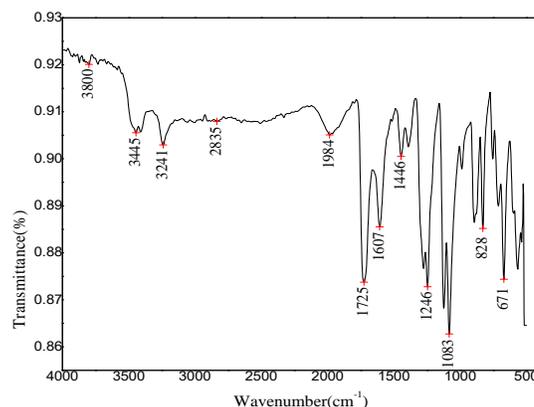


Figure 2: FTIR Spectrum of Tartaric acid monohydrate crystal

absorption of O-H stretching appears as a broad band between 3445 and 2835 cm^{-1} . A free hydroxyl stretching vibration is observed at 3800 cm^{-1} . In this spectrum a weaker C-H stretching bands at 2835 cm^{-1} , 3241 cm^{-1} and 3445 cm^{-1} are superimposed upon the broad O-H band. The C=O stretching band occurs at 1725 cm^{-1} . The peak at 1446 cm^{-1} corresponds to C-O-H in plane bending and 1246 cm^{-1} is due to CO stretching. The absorption peaks characterizing different functional groups are given in the Table 1, and they are very good agreement with the reported values in literature [8]. The ultraviolet visible near infrared (UV-Vis-NIR) transmittance curve for the tartaric acid monohydrate single crystal is shown in the Fig.3. In the transmittance curve of tartaric acid monohydrate single crystal, the lower cut-off wavelength is about 240 nm and it is observed that there is a steady transmittance in the visible region. The transmittance in the visible region is above 90 % and the maximum transmittance of the grown crystal is 96 % which is also found to be steady throughout the near infrared region. This spectroscopic technique is not useful below 200 nm since the oxygen

absorbs strongly at 200 nm and below. The region below 200 nm is called vacuum ultra violet region [9].

Table 1: Frequencies of the fundamental vibrations of Tartaric acid monohydrate crystal

Frequency in wave number (cm ⁻¹)	Assignment of vibration [8-10]
3800	free hydroxyl stretching vibration
3445	weaker C-H stretching bands
3241	O-H stretching
2835	weaker C-H stretching bands
1984	C=O stretching
1725	C=O stretching band
1607	C=C stretching
1446	C-O-H in plane bending
1246	CO stretching
1083	CH ₂ rocking
828	OH out of plane bending
671	COO bending

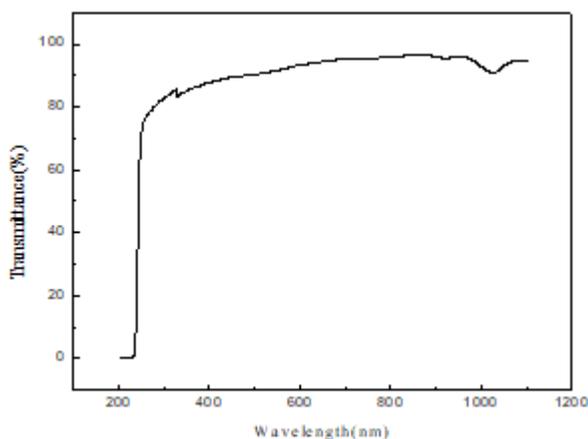


Figure 3: UV-Vis-NIR Transmittance spectrum of Tartaric acid monohydrate crystal

In the microhardness testing, the diagonal length of the indentation corresponding to the load applied on the crystalline material was measured. Fig.4 shows the measurement of microhardness as a function of load in gram. It is observed from the graph plotted between load and microhardness that the hardness value increases with the increase of load and attain maximum when 90 gram load is applied and thereafter it decreases. This is due to the reason that when load is applied, the atoms are dislocated along the slip plane and it increases with increase of load up to a certain load. The dislocated atoms restrict further flow of dislocation when the load applied is more. Thereafter the crystal undergoes plastic deformation and finally it breaks. The maximum hardness of the crystal is found to be 237 kg/mm² at 90 gram load.

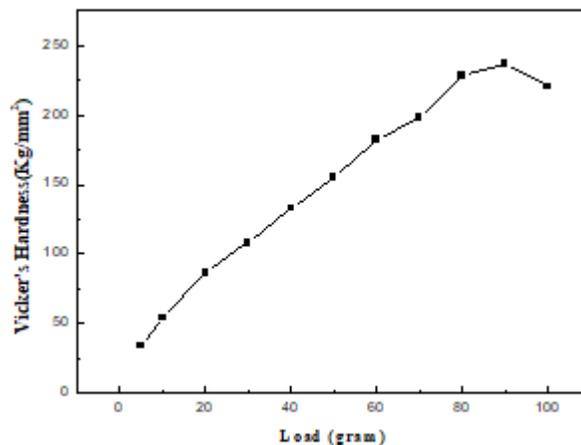


Figure 4: Microhardness of Tartaric acid monohydrate crystal

Work hardening is the strengthening of a material by plastic deformation. This strengthening of a crystalline material occurs due to dislocation of atoms movements within the crystal structure. The material becomes stronger and more difficult to undergo further deformation as the material requires more stress to produce additional plastic deformation. In order to find the increase in strength that accompanies plastic deformation of the grown crystal, Work hardening coefficient (n) was calculated using the Meyer's relation $P = ad^n$, where P is the applied load, d is the diagonal length of the indentation and a is the constant for the given material. Fig.5 shows the graph showing the relationship between logarithmic value of the load P applied on the crystal and the diagonal length d of the indentation. From the graph, the work hardening coefficient was calculated by taking a slope and it was found to be 5. According to Onitsch [11] n lies between 1 and 1.6 for hard materials and it is more than 1.6 for soft materials, further if $n > 1.6$, then the microhardness H_v increases with the increase of load [12, 13] and vice versa. Since the 'n' value is 5, it is suggested that the grown tartaric acid monohydrate crystal is a softer material. From the measurement of microhardness, yield strength can be calculated using the relation [14, 15] $\sigma_y = (H_v/3)(0.1)^{n-2}$, where σ_y is the yield strength, H_v is the hardness of the material and n is the logarithmic exponent. According to the relation, the yield strength of the tartaric acid monohydrate single crystal was calculated as 79 MPa, and hence the grown crystal has relatively low mechanical strength.

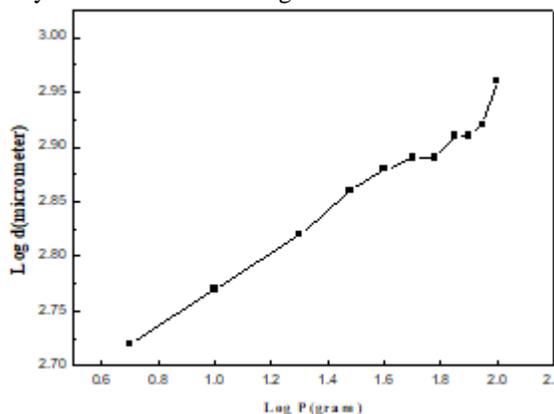


Figure 5: Plot of log P and log d of Tartaric acid monohydrate crystal

The thermogravimetric and differential thermal analysis curves for the sample are shown in the Fig.6. In the thermogravimetric curve, weight loss about 9.58 % occurs at 110.5 °C temperature, which is due to the devoid of water content in it. The corresponding sharp endothermic peak obtained at this temperature in the differential thermal analysis curve also indicates the evaporation of water molecules. The next stage between the temperature 217.3 °C and 248.3 °C with a loss of 86.7 % is attributed to the decomposition of tartaric acid compound. The decomposition of the compound starts from the temperature 217.3 °C and ends at 248.3 °C, which is indicated by the another sharp endothermic peak obtained at the temperature 248.3 °C in DTA curve. The remaining few percentage of mass of the tartaric acid exists as a residual mass at the temperature above 248.3 °C. In the differential scanning calorimetric curve shown in the Fig.7, there are two major endothermic peaks obtained at 113.3 °C and 217.3 °C. The area covered at the peak 113.3 °C indicates the amount of heat required to evaporate water content in the title compound, which is about 82.55 J/g. Tartaric acid monohydrate require 389.3 J/g heat to decompose its major content, which is shown in the area covered at the endothermic peak 217.3 °C. There is no phase change observed from the differential

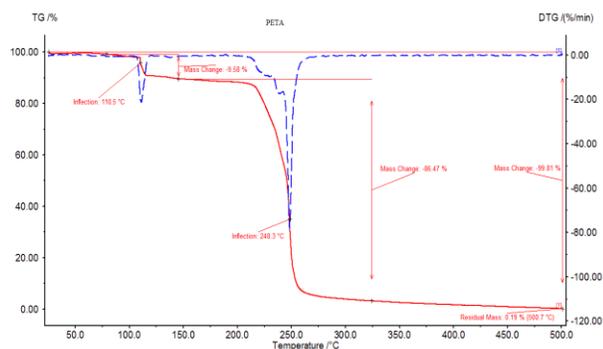


Figure 6: TGDTA curves of Tartaric acid monohydrate crystal

Scanning calorimetric curve and differential thermal analysis curve before the decomposition of the sample.

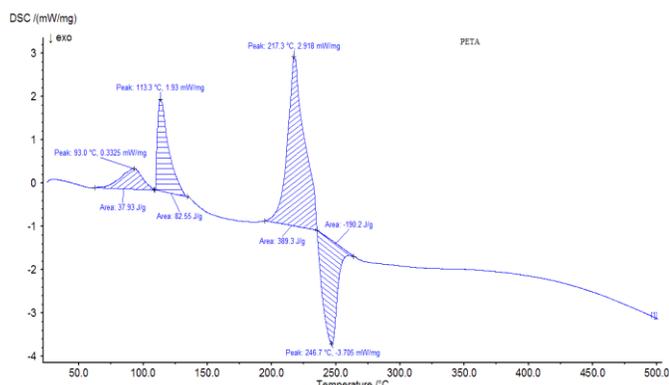


Figure 7: DSC curve of Tartaric acid monohydrate crystal

5. Conclusions

Tartaric acid monohydrate single crystal an organic compound can be grown by slow solvent evaporation technique at room temperature. The compound was confirmed by single crystal X-ray diffraction and various functional groups present in the crystal were identified using FTIR spectrum. Since it is centrosymmetric crystal, it was not supported for nonlinear optical effect even it is a combination of two optically active enantiomer in right proportion. The maximum transmittance of the grown crystal obtained is 96 %, which is in the near infrared region. From the investigation of microhardness, the grown crystal is soft material. The material does not undergo phase change below the decomposition temperature of the tartaric acid for water molecules at 110.5 °C.

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References

- [1] S. A. Martin Britto Dhas, S. Natarajan, Cryst. Res. Technol. 42 (2007) 471 – 476.
- [2] Mohd Shkir, Haider Abbas, Spectrochim. Acta Part A, 118 (2014) 172–176.
- [3] T. Prasanyaa, V. Jayaramakrishnan, M. Haris, Optik, 125 (2014) 732–736.
- [4] G. Saravana Kumar, P. Murugakoothan, Optik, 126 (2015) 68–73.
- [5] V. Sheelarani, J. Shanthi, Optik, 127 (2016) 2946–2949.
- [6] M.I. Baig, Mohd Anis, G.G. Muley, Optical Materials 72 (2017) 1–7.
- [7] Jing-Jing Nie, Duan-Jun Xu, Jing-Yun Wu, M.Y. Chiang, Acta Cryst. E, 57 (2001) o428–o429.
- [8] M. Robert Silverstein, X. Francis Webster, J. David Kiemle, Spectrometric identification of organic compounds John Wiley & sons, United States of America, 2005.
- [9] Y. R. Sharma, Elementary Organic Spectroscopy, S. Chand & Company Ltd, New Delhi, 2007.
- [10] M. Esthaku Peter, P. Ramasamy, Spectrochim. Acta Part A, 75 (2010) 1417–1421.
- [11] Onitsch, E. M. Microscope, 1950, 95, 12.
- [12] R. Ramesh Babu, S. Kumaresan, N. Vijayan, M. Gunasekaran, R. Gopalakrishnan, P. Kannan, P. Ramasamy, J. Cryst. Growth, 256 (2003) 387–392.
- [13] N.P. Rajesh, V. Kannan, M. Ashok, K. Sivaji, P. Santhana Raghavan, P. Ramasamy, J. Cryst. Growth, 262 (2004) 561–566.
- [14] P. Cahoon, W.H. Broughton, A.R. Kutzuk, Metall. Trans., 2 (1971) 1979.
- [15] M. Esthaku Peter, P. Ramasamy, Adv. Mater. Lett. 7 (2016) 83–88.

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