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ISSN: 0976-3031

International Journal of Recent Scientific Research
Vol. 4, Issue, 9, pp.1332- 1336, September, 2013

International Journal of Recent Scientific Research

RESEARCH ARTICLE

SINGLE CRYSTAL OF SODIUM HYDROGEN L-TARTRATE MONOHYDRATE: GROWTH AND CHARACTERISTICS

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ARTICLE INFO

Article History:

Received 13th, August, 2013
Received in revised form 27th, August, 2013
Accepted 17th, September, 2013
Published online 30th September, 2013

Key words:
Slow evaporation method, Metal-Organic compound, Thermal analysis, Dielectric studies and Microhardness

ABSTRACT

Single crystals of Sodium Hydrogen L-Tartrate Monohydrate (SHTM) were grown by slow evaporation solution growth technique using deionized water as solvent. The grown crystal was confirmed by single crystal X-ray diffraction studies. The presence of the functional groups was identified by FTIR measurement. The thermal property of the grown crystal was studied by TG-DTA analysis. The dielectric behavior of the crystal was investigated with different frequencies and temperatures. The Vicker's micro hardness test was also carried out to test the mechanical stability and the hardness parameters are determined.

INTRODUCTION

Physicists, chemists, material scientists and crystal engineers identify new Non-linear optical crystals. Nonlinear optical (NLO) materials have a great impact on information technology and industrial applications. The new development of techniques for growth of artificial materials has dramatically contributed to this evolution. Semi-Organic crystals exist with the advantage of both organic and inorganic compounds having good NLO, mechanical and thermal properties. Semiorganic materials are metal- organic coordination complexes in which the organic ligand plays a dominant role for the NLO effect. Organometallic compounds which contain metal and organic ligands linked by coordination bond. The structure of the organometallic compound can be varied by changing the metal, coordination number and ligands and so on. The variety of molecular structure tune the electronic properties of the molecules, and hence to exploit the linear and nonlinear optical properties. We are chosen here the Non-aromatic organic acids: Tartaric acid and inorganic salt: Sodium nitrate to get Metal-Organic sodium hydrogen L-Tartrate monohydrate crystal. In tartaric acid single proton ionization is easy, as the resulting mono tartrate can have hydrogen bonding between -COO- and -COOH. Once the proton is ionized, its place can be replaced by any other ions like Na+. A number of tartaric acid complexes are known to possess NLO property [1–3]. The crystal structure of sodium hydrogen L-Tartrate monohydrate was reported by R. C. Bott et al and Y.Kubozono et al [4,5]. There is no systematic studies appear to have been carried out for the crystals of sodium hydrogen L-Tartrate monohydrate up to our knowledge. In the present studies, our aim is to investigate the properties of the single crystals of SHTM. The crystal has been grown by the slow evaporation technique at room temperature, and the growth aspects of SHTM, the results of single X-ray diffraction (XRD), Fourier transform infrared (FTIR) analyses, dielectric studies have been studied. Thermal and mechanical behavior of the crystal has also been discussed.

Experimental procedure

Synthesis and crystal growth

Single crystals of SHTM have been grown by slow evaporation method from their aqueous solutions using deionized water as a solvent. SHTM salt was synthesized using analytical grade of L-tartaric acid and sodium nitrate in a stiochiometric ratio of 1:1.The required quantities of tartaric acid and sodium nitrate were estimated from the following reaction:

$$C_4H_6O_6 + NaNO_3 \rightarrow NaHC_4H_4O_6{\cdot}H_2O + HNO_3 \quad (1)$$

The calculated amounts of the reactants were thoroughly dissolved in deionized water and stirred well for about 1 hour using a magnetic stirrer to obtain a homogeneous solution. Then the solution was filtered well to remove the suspended impurities and allowed to crystallize by slow evaporation techniques. The crystal was further purified by repeated re-crystallization process. Thereby good colorless crystals of dimensions 1.2×0.4×0.2 cm^3 were obtained in 35-40 days, which is shown in (Fig.1).

MATERIAL CHARACTERIZATIONS

The grown single crystals have been subjected to various characterization methods. The grown crystals have been confirmed by using BRKER axs SMART APEXII diffractometer. The functional groups were confirmed by Fourier transform infrared spectra using SHIMADZU-8400S Spectrophotometer. The mechanical properties have been tested from Vickers micro hardness measurements using Shimadzu HMV-2T. The thermal behavior has been analyses by TGA/DTA studies using NETZSCH STA 409 PC. Transparent polished crystals of rectangular dimension 7.28x1.48x1.68 mm^3 was selected for dielectric studies using HIOKI 3532-50 LCR HITESTER.

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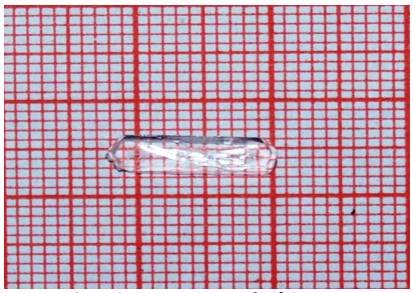

Fig.1 As-grown crystal of SHTM

Single Crystal XRD

The X-ray data were collected using BRKER axs SMART APEXII diffractometer. It is observed from the X-ray diffraction data that the SHTM crystal is orthorhombic in structure with space group $P2_12_12_1$.The collected data of lattice cell parameters are a= 7.22 Å, b= 8.66 Å, c= 10.58 Å and V=662 $Å^3$. The calculated lattice parameter values are tabulated in Table 1 and it agrees well with the earlier reported values [4,5].

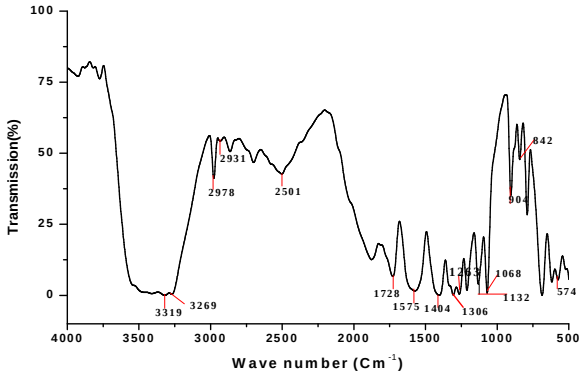

Fig .2 FTIR spectrum of SHTM single crystal

FTIR study

Fourier transform infrared spectra of SHTM crystal was carried out in the middle IR region between 4000 and 400 cm^{-1} using SHIMADZU-8400S Spectrophotometer and the spectrum is shown in Fig.2. The vibration spectrum of a molecule generally consists of two major regions (i) Group frequency region (ii) Finger print region. Group frequencies are vibrations that are associated with certain structural units such as $-CH_3$,$-NH_2$, -C≡ N etc and appear fairly constant regions in the spectrum. The molecules having similar groups show their vibration in the form of bands is called finger print region. The infrared spectrum of SHTM crystal is shown in Fig.2. The broad peak at 3404 cm^{-1} is due to the presence of O-H stretching in the carboxyl group. The sharp peak observed at 1737 cm^{-1} indicates the presence of C=O. The peak at 1305 cm^{-1} is attributed to the C-H in-plane bending. The peak at 1404 cm^{-1} corresponds to the vibration of carboxyl ion. The other functional groups present in the crystal are summarized in Table 2.

Thermal analyses

Thermal analyses were performed on the grown crystals to study the thermal stability and melting point. Thermogravimetric (TG) and differential thermal analyses (DTA) are of immense importance as for as the fabrication technology is concerned, as they provide thermal stability of the material for fabrication where a considerable amount of heat is generated during the cutting process. The TGA analysis of SHTM was carried out from room temperature to 600 □C in the nitrogen atmosphere using NETZSCH STA 409 PC with the heating rate of 10 □C/min. The different stages of weight loss are clearly given in TGA and DTA traces are shown in Fig 3.

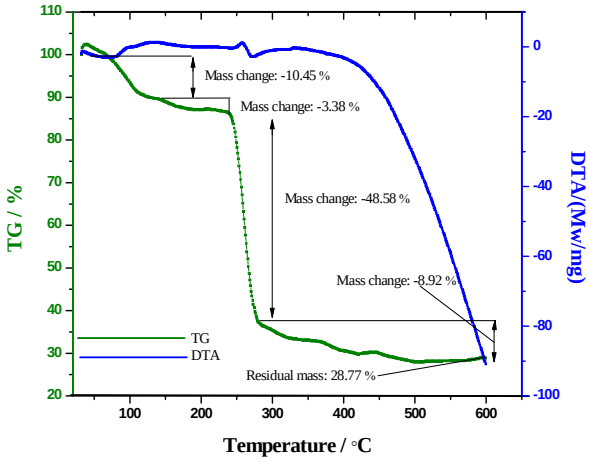

Fig.3 TG-DTA analysis of SHTM crystal

From the TGA spectrum it is inferred that there is 10.45 % weight loss owing to loss of water of crystallization. The major weight loss of 48.58 % due to the decomposition of organic molecules associated with SHTM. The curve saturate at 500 □C and giving a residue equal to 28.77 %. From the DTA curve it is observed that the compound is stable and there is no phase transition. However, there is an endothermic peak occurred at 240 □C, which is due to the melting of the material.

Dielectric measurements

Dielectric properties of NLO materials are important for their fast switching times in electro-optic applications. There are four types of polarization occur by applied electric field over a material ie., electronic, ionic, orientation and space charge polarization. At low frequencies of the order of power frequencies all the four types of polarization present. So that dielectric constant increases by the high value of total polarization.

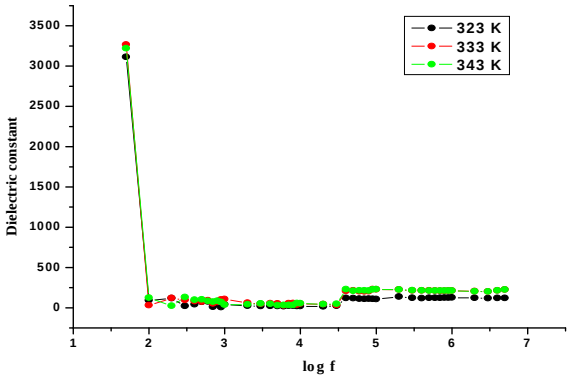

Fig.4a Dielectric constant of SHTM with log frequency

As the frequency is increased space charge, orientation, ionic polarization become less effective and the total polarization is very small. Then dielectric constant decreases.Dielectric constant and dielectric loss (tan δ) values have been found using HIOKI 3532-50 LCR HITESTER in the frequency range 50 Hz to 5

MHz. Dielectric studies was performed from 50 to 70 □C in the range of 10 □C. Rectangular shaped crystal of dimension (l = 7.25 mm, b = 2.48 mm and t = 1.68 mm) has been pasted with conductive silver paint for metallic contacts.

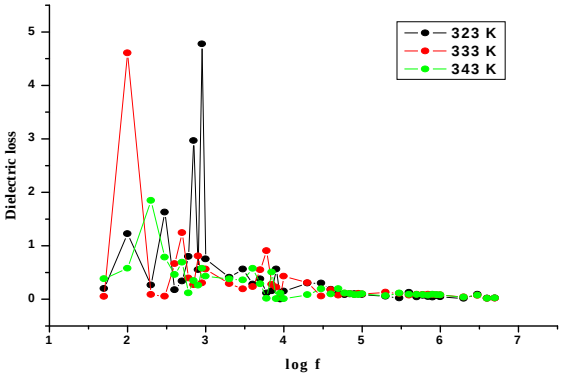

Fig.4b Dielectric loss of SHTM with log frequency

The dielectric constant of SHTM was found by measuring the capacitance of the samples and calculating the dielectric constants assuming that each sample behave like a parallel plate capacitor. From the capacitance data, the dielectric constant at each temperature is calculated using the formula

$$\varepsilon_r = Ct/\varepsilon_0 A \quad (2)$$

Where ε_o is the permittivity of the free space, C is the capacitance, t is the thickness of the sample crystal and A is the area of the cross section. The variations of dielectric constant and dielectric loss as a function of log frequency at different temperatures are shown in Fig. 4a and 4b. It is found that the dielectric constant decreases with increasing frequency and increases with temperature at high frequencies.

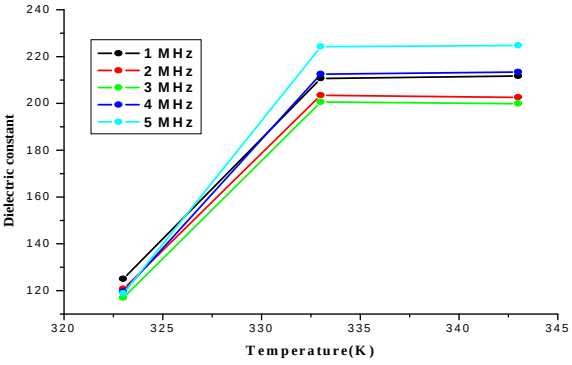

Fig.4c Temperature dependence of dielectric constant of SHTM

At low frequencies, some fluctuation is there in the value of dielectric constant with temperature. The dielectric constant of the sample is found to be 3112.42 at 50 Hz and it decreases to 118.79 at 5 MHz. Dielectric losses also decreases with increasing frequency. In the high frequency region, both the dielectric constant and dielectric loss attain almost constant values. A similar trend is seen for all the recorded temperatures.

Mechanical property

Hardness is one of the important mechanical properties of the materials. It can be used as a suitable measure of the plastic properties and strength of a material [6]. Hardness is an ability of a crystal to resist a structural breakdown under an applied stress. This resistance is an intrinsic property of the crystal.

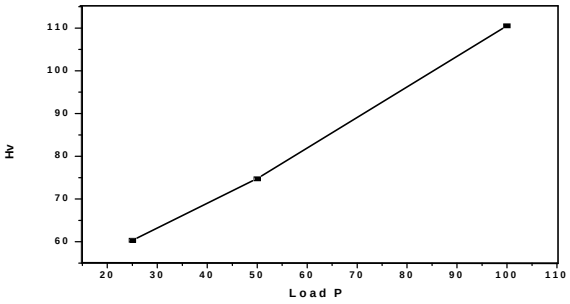

Fig.5a Microhardness Curve of SHTM crystal

Hardness is generally taken as a ratio of applied load to the area of indentation. The indenter is usually made of a material much harder than that being tested; e.g. hardened steel, sintered tungsten carbide or diamond [7]. The microhardness parameters were determined using Shimadzu HMV-2T micro hardness tester fitted with a Vicker's diamond indenter attached to a microscope. It were done for applied loads (P) varying from 25 to 100 gm. The flat surfaces of the grown crystal were subjected to this study. The distance between any two consecutive indentations was kept at more than thrice the diagonal length of the indentation mark. Thus surface effects were independent of one another.

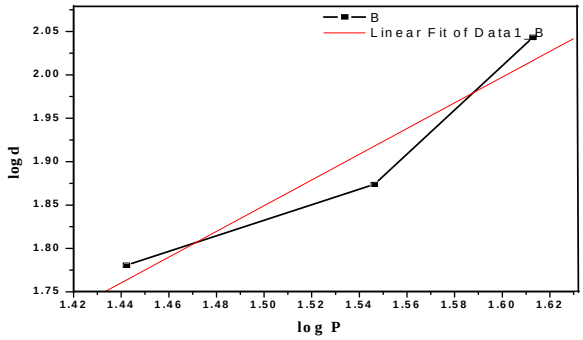

Fig.5b Plot of log P vs. Log d of SHTM crystal

The impressions were approximately square. Several impressions were made for each load and the diagonals (d) were averaged. The Vicker's hardness numbers (Hv) were calculated using the formula:

$$H_v = 1.8544\, P/d^2\ kg/mm^2 \quad (3)$$

Where P is in g, d is the average value of two indentation diagonal lengths in mm and Hv in kg mm^{-2}.

Table.1 Crystallographic data of SHTM crystal

Chemical formula	$NaHC_4H_4O_6{\cdot}H_2O$
Crystal System	Orthorhombic
Space group	$P2_12_12_1$
a(Å)	7.22
b(Å)	8.66
c(Å)	10.58
α(deg)	90
β(deg)	90
γ(deg)	90
Volume($Å^3$)	662
Crystal color	Colorless

The Vickers microhardness (H_V) is calculated using this formula. A graph was plotted between hardness number (Hv) and applied

load P as shown in Fig.5a. From the profile, it is observed that the hardness increases with increase in load satisfying reverse indentation size effect (RISE). A plot of log P vs.log d, fitting data before cracking gives a straight line (by least square fitting), Which is in good agreement with Meyer's law. It is shown in Fig.5b.The value of n is found from the slop of the graph and the value is 1.4815. According to Onitsch, the material is regarded as hard material for 1.0 < n < 1.6 and n > 1.6 for soft materials **[**8**]**. In the present study, n is found to be less than 1.6, thus confirming that SHTM is a hard material. From Kick law, the load P is direct proportionality to the size of the indentation d^n results:

$$P = K_1 d^n \qquad (4)$$

Where k_1 and n are constants for a particular material. It suggests constancy of Hv with increase in load.

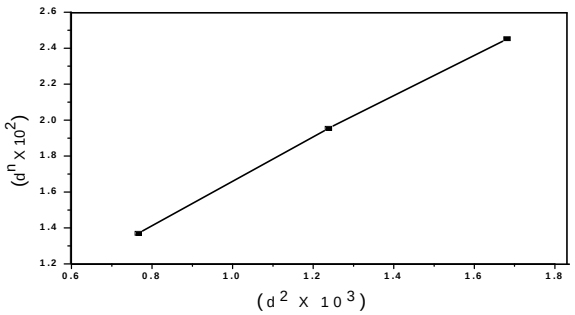

Fig. 5c A plot showing d^n vs. d^2 of SHTM crystal

At low values of the applied load, the Kick law is no more observed and the measured hardness begins to be dependent on the load. The Hays-Kendall model has modified the Kick law by including a factor would be obeyed at whatever load.

Table.2 Frequencies of the fundamental vibrations of SHTM

Wave number	Functional groups
3410	O-H stretching
3319	Vibrations of H_2O
3269	Carboxylic acids O-H stretch
2978	CH_2 vibration
2931	C–H stretching superimposed upon O–H
2501	Carboxylic acid O-H stretch
1728	C=O stretching
1575	C=O vibration mode
1404	Vibrations of COO^-
1305	C-H in-plane bend
1263	δ (C-H)+ π (C-H)
1132	δ (C-H)+ π (C-H)
1068	–OCH stretching mode
904	O-H….O out-of-plane bending vibrations

That is the amount of plastic deformation 'W' called sample resistance pressure during the indentation process is smaller than the applied load P [9] . Hence the Kick law should be written as follows:

$$P - w = Kd^2 \quad (5)$$

Substituting the expression of Eq. (4) for P in Eq.(5),we have

$$W = K_1 d^n - K_2 d^2\, d^n = (K_2/K_1)\, d^2 + (W/K_1) \quad (6)$$

Where P is the pressure in Pascal, D is the diameter of the indentation, k_1 is the standard hardness constant and n is the Meyer index or work-hardening coefficient. The slope of d^n versus d^2 (Fig.5c) yields (k_2/k_1) and the intercept is a measure of (w/k_1).From the hardness value, the yield strength σ_v can be calculated using the relation.

$$\sigma_v = \frac{H_v}{2.9}[1-(n-2)]\left[\frac{12.5(n-2)}{1-(n-2)}\right]^{(n-2)} \quad (7)$$

The hardness parameters of SHTM crystals such as, n, k_1, k_2, w, and σ_v were calculated using these relations.and presented in Table.3.

Table.3 The hardness parameters for the SHTM single crystal

Parameters	Values
n	1.4815
K_1 (Kg/m)	2.3610
K_2 (Kg/m)	0.2000
W(m)	0.5008

The elastic stiffness constant is calculated using Wooster's empirical formula, given by

$$C_{11} = H_V^{\frac{7}{4}} \qquad (8)$$

The calculated stiffness constant for a load from 25 gm to 100 gm has been calculated and is given in Table.4.

Table.4 Mechanical properties of SHTM crystal

Load P(g)	d (mm)	H_v (Kg/mm^2)	C_{11} (GPa)	σ_v(MPa)
25	27.68	60.35	12.8059	145.92
50	35.19	74.8	18.6446	180.86

CONCLUSION

Metal-Organic crystals of sodium hydrogen L-Tartrate monohydrate crystals (SHTM) were grown from slow evaporation technique. Single crystal X-ray diffraction study shows the crystal belongs to orthorhombic crystal system with space group $P2_12_12_1$.The FT-IR spectrum reveals the functional groups of the grown crystals. The thermal studies show that melting point of the crystal is 240 □C. The dielectric constant and dielectric loss were studied as a function of frequency at room temperature**.** It shows that the dielectric constant increases with increase in temperature. The mechanical properties were carried out to understand the hardness parameters and stiffness constant of the grown crystals.

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