Growth, Linear and Nonlinear Optical Studies of D-Tartaric Acid Crystal

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Abstract

A single crystal of D-Tartaric acid, a stereoisomer of tartaric acid, has been grown by a slow solvent evaporation technique. Good crystals to be used for optical testing were harvested after multiple recrystallizations, whose maximum size is 30x20x4mm^3. In view of finding second harmonic generation efficiency and properties supporting for a nonlinear optical device, the grown crystals were subjected to various characterizations. Firstly, the compound was confirmed by single crystal and powder X-ray diffraction analysis and thereafter further studies were undertaken. Various possible functional groups available in the grown crystalline compound were identified using Fourier transform infrared analysis and reported. The second harmonic generation, a nonlinear optical property of a crystal, was studied and compared with standard KDP crystal. The percentage of linear optical transmittance in the ultraviolet, visible and infrared radiation of wavelength ranging from 200 to 1100 nm was studied and explained in detail. Thermal studies such as Thermogravimetric and Differential thermal analysis were carried out to find the thermal stability of the crystalline material. 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: X-ray diffraction, growth from solutions, organic compounds, nonlinear optic materials, harmonic generators.

Introduction

Photonic materials are the key elements for the scientific growth and advanced laser technology in new millennium. During the past two decades, extensive theoretical and experimental investigations have been made on organic nonlinear optic (NLO) materials due to their high second harmonic generation (SHG) efficiency [**1-3**]. Nonlinear optics is playing a major role in the emerging photonics and optoelectronics technologies. New materials possessing high nonlinear optical frequency conversion efficiency find a significant impact on laser technology. Tartaric acid is an optically active and one of the important carboxylic acid in organic compounds. It is also called as dihydroxy butanedioic acid which is in the form of chiral molecule, and existing as three stereoisomers: D-tartaric acid, L-tartaric acid and meso-tartaric acid [**4**]. In view of developing SHG material in the enantiomer of this group, an attempt was done on D-Tartaric acid. Because, chirality plays a vital role in producing stable second order nonlinear optical material. One of the important characteristics of a molecule having NLO property is noncentrosymmetric nature. These chiral molecules have such a property without vanishing electric-dipole, which response greatly second order polarization [**5**]. Many reports towards the study of nonlinear properties on pure L-Tartaric acid and combined with amino acid and other organic compound [**6-9**]. Since the title compound is also an optically active material like L-Tartaric acid, an attempt on crystal growth from solutions was executed and made to reveal its second harmonic generation effect including other required properties for optical device.

Crystal growth

The organic compound D-tartaric acid was grown in the form of single crystal by slow solvent evaporation

technique at room temperature. Commercially available D-tartaric acid of sufficient quantity (50 gram) was taken in a well cleaned glass beaker and dissolved in distilled water. Solvent was added little by little until it becomes dissolved completely. Saturated aqueous solution of D-Tartaric acid was prepared at room temperature and it was stirred for 5 hours in order to make a homogeneous mixture of solute in the solvent. The pH of the solution was measured by a pH indicator and the value was noted. The temperature of the solution preparation and pH value of the solution were 28ºC and 2 respectively. Then the solution was filtered by using Whatman filter paper and it was kept in an undisturbed place for facilitating crystal growth at room temperature. The solution was allowed for slow evaporation by closing the beaker using perforated polythene cover. A small nucleus was observed to form at the bottom of the solution after a few days. After 20 days, large and less transparent crystals were grown. But after 3 times recrystallization, large and good transparent crystals were obtained. The grown crystals were harvested from the mother solution and dried in a dust free place. The photograph of the grown crystals is shown in the **Fig. 1**.

Fig. 1. Photograph of D-Tartaric acid crystal.

Experimental methods

The Nonlinear optical crystals D-Tartaric acid grown by slow evaporation technique was subjected to various studies to reveal its properties. Its crystal structure was determined by both single crystal X-ray diffraction and powder X-ray diffraction and compared with the reported cell parameter. Single crystal X-ray diffraction analysis was performed by a Bruker AXS Kappa APEX II single crystal CCD diffractometer equipped with graphite monochromated Mo (Kα) radiation of wavelength 0.7107 Å. Powder X-ray diffraction (PXRD) of the grown D-Tartaric acid crystal was recorded using Seifert Dyz 2002 model powder X-ray diffractometer with CuKα (λ = 1.540598 Å) radiation for revealing crystalline nature and comparing structural similarity with the existing pattern. The crystalline sample was crushed into fine powder and it was used for scanning over the range of 10-70° with a scanning rate of 1°/minute. The intensity of the diffracted X-ray radiation was recorded with respect to 2θ and the obtained peaks were indexed. Thereafter the diffracted pattern was compared with already reported PXRD pattern. Infrared spectroscopy is widely used in both research and industry as a simple and reliable technique for measurement, quality control and dynamic measurement. This technique works on the fact that bonds and groups of bonds vibrate at characteristic frequencies. A molecule that is exposed to infrared rays absorbs infrared energy at frequencies which are characteristic to that molecule. In order to analyze the presence of functional groups in D-Tartaric acid crystals qualitatively, Fourier transform infrared spectrum was recorded between 4000 and 450 cm^{-1} using Perkin-Elmer spectrum one FTIR spectrometer. To determine the linear optical properties transmittance, optical band gap and confirming the suitability of D-Tartaric acid single crystal for optical applications; the UV-Vis-NIR transmission spectrum was recorded in the range of 200 to 1100 nm using Perkin Elmer Lamda 35 UV/VIS spectrometer. The crystal of 3 mm thickness was used for recording the spectrum.

The Second Harmonic generation (SHG) is used as an important tool to evaluate qualitatively the bulk homogeneity of the samples under investigation [**10**]. It is a relevant technique for frequency conversion effect in a laser device. The SHG behavior of D-Tartaric acid sample of particle size 150 micron, which was prepared by a sieve with the same size of mesh, was analyzed using Kurtz-Perry powder technique. Thereafter it was compared with the standard pure KDP crystal in powder form with same range of size. A high intense Nd: YAG laser source was used whose beam wavelength and energy is 1064 nm and16.5 mJ/pulse respectively. The corresponding input pulse and pulse width is 1mV/pulse and 10 ns. The laser radiation was allowed to pass through the sample taken in the form of powder in a microcapillary tube. Pure KDP was used as reference sample. Both the reference and test samples had uniform particle size of 150 micron. The experiment was carried out in pure KDP and later in the D-Tartaric acid sample. Thermal properties of D-Tartaric acid single crystal were studied by Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA). These were carried out between 30°C and 990°C in nitrogen atmosphere at a heating rate of 10°C/min using SDT Q600 V20.9 Build 20 TG/DTA instrument by stepwise isothermal method. It is very essential to reveal the mechanical properties of the grown crystal for nonlinear optical device applications. So mechanical properties of the grown nonlinear optical D-Tartaric acid crystals were analyzed using HMV2T Microhardness testor. While the material is handled for device fabrication, it should possess sufficient resistant to scratching and indentation and hence the Vicker's microhardness studies were undertaken. The Vicker's microhardness values were calculated from the standard formula $H_v = 1.8544\ P/d^2$ kg/mm^2, where P is the applied load and d is the mean diagonal length of the indentation.

Results and discussions

The single crystal X-ray diffraction data analyzed by full-matrix least squares refinement method of D-Tartaric acid indicate that the crystal is monoclinic in structure, with space group of $P2_1$. The unit cell parameter values are found to be a = 7.716(2) Å, b = 6.006(3) Å, c = 6.227(1) Å, β = 100.14° with cell volume V = 288.573 $Å^3$. The results are in good agreement with the reported JCPDS crystallocraphic data [**11**]. **Fig. 2** shows the powder XRD pattern of the grown D-Tartaric acid, which is similar to the reported pattern available in JCPDS data. The XRD pattern was indexed with different plane against the peak. The intensity of the peak obtained in this pattern indicates the good crystalline nature of that system. The Fourier transform infrared spectrum of D-Tartaric acid is shown in the **Fig. 3**. Carboxylic acid exists as dimmers due to strong hydrogen bonding. Due to the presence of strong hydrogen bonding, a free hydroxyl stretching vibration is observed at the frequency 3406 cm^{-1}. A strong and broad stretching vibration obtained between 3333 cm^{-1} and 2615 cm^{-1} belongs to O-H group for bicarboxylic acid D-Tartaric acid [**12**]. The stretching vibration corresponds to 2935 cm^{-1} is observed to superimpose with O-H broad vibration. Dimeric carboxylic C=O stretching is found to be at 1740 cm^{-1} and C-O-H in-plane bending vibration takes place at 1400 cm^{-1}. The C-O stretching for bicarboxylic acid occurs at 1257 cm^{-1}. The out of plane bending of the C-O-H lies at the frequency 943 cm^{-1}. This is the characteristic band in the infrared spectra of bicarboxylic acid. Frequency of vibration at 1086 and 791 cm^{-1} is due to the CH_2 rocking and frequency of vibration at 578 and 485 cm^{-1} corresponds to the C-H wagging. **Table 1** shows the frequency of vibration for different functional group assignments.

Table 1. Frequencies of the fundamental vibrations of D-Tartaric acid crystal.

Frequency in wavenumber (cm^{-1})	Assignment of vibrations [12-16]
3406	Free hydroxyl stretching vibration
3333	O-H stretching
2615	O-H stretching
1740	C=O Strong Stretching
1400	C-O-H in-plane-bending
1257	C-O strong stretching
1209	C-O stretching
1131	C-O strong stretching
1086	CH_2 rocking
993	CH_2 bending
943	C-O-H out of plane bend
874	C-O-H out of plane bend
791	CH_2 rocking
736	C-H out of plane bending
671	COO bending
578	C-H wagging
485	C-H wagging

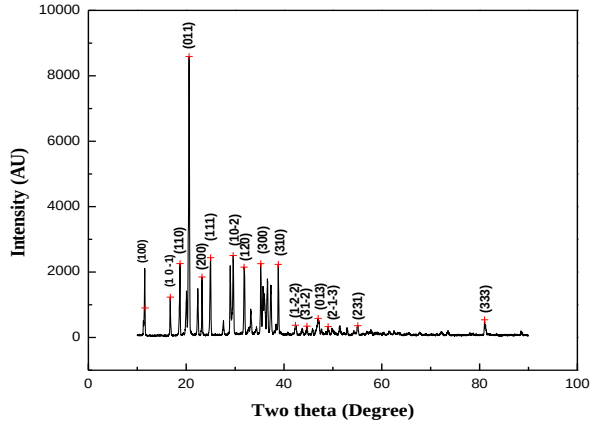

Fig. 2. Powder XRD pattern of D-Tartaric acid crystal.

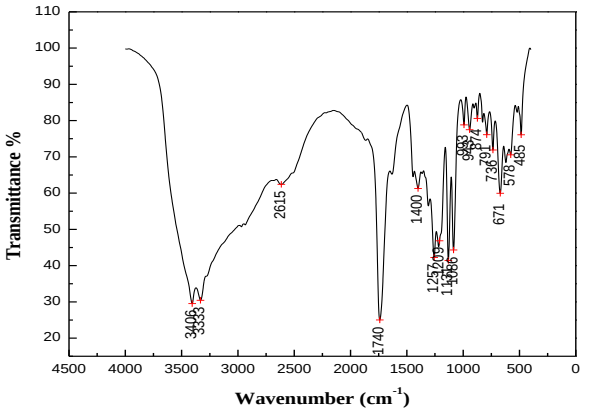

Fig. 3. FTIR Spectrum of D-Tartaric acid crystal.

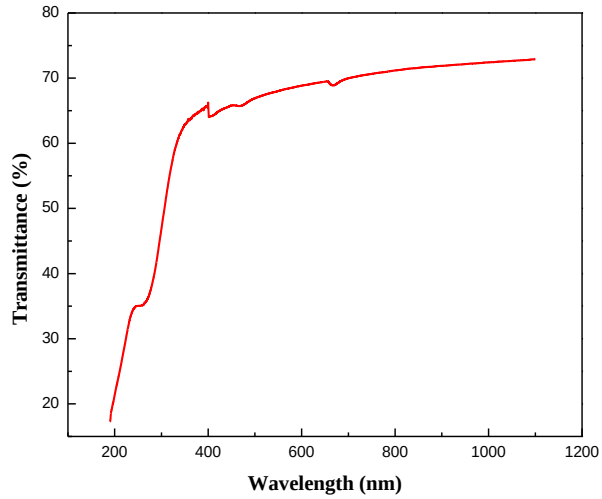

Fig. 4. UV-VIS-NIR Transmittance spectrum of D-Tartaric acid crystal.

Fig. 4 shows the resultant transmittance curve, in which it is observed that there is a steady transmittance in the visible region. The transmittance in the visible region is above 70 % and the maximum transmittance of the grown crystal is 73 %. The spectrum indicates that the lower cut-off wavelength is about 250 nm. It is worth noting that the transparency range for D-Tartaric acid single crystals is sufficiently large for any optical application. The optical band gap (E_g) 5.1 eV was evaluated from the absorption spectrum using optical

absorption coefficient 'α' by mathematical calculation. It was estimated by plotting a curve between $(\alpha h\upsilon)^2$ and photon energy $h\upsilon$ as shown in the **Fig. 5**.

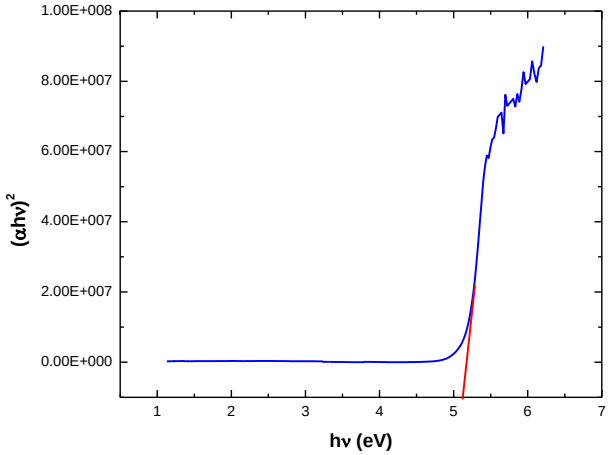

Fig. 5. Plot of $(\alpha h\upsilon)^2$ vs. photon energy for D-Tartaric acid crystal.

The curve was extrapolated from the linear portion near the onset of absorption edge to the x-axis.

$$\alpha = \frac{2.3036 \log(1/T)}{t}$$

where t is the thickness of the sample used for finding the linear optical transmittance and absorption. The D-Tartaric acid sample, packed in a microcapillary tube in the form of very fine powder, was placed in the path of Nd-YAG laser beam. The beam voltage of the transmitted radiation was 24 mV, when pure KDP crystalline sample in the form of powder was used as a reference material. But the transmitted beam voltage through the D-Tartaric acid sample was measured as 23 mV. Hence the SHG efficiency is just equal to that of the standard KDP crystal. The transmitted beam from the sample holder was observed in green color and the wavelength of the beam was 532 nm. From this observation and measurement made on the beam voltage and compared with the standard NLO material pure potassium dihydrogen phosphate, D-Tartaric acid is a good candidate for the conversion of frequency in nonlinear optical device. The respective TGA trace for D-Tartaric acid single crystal is shown in the **Fig. 6**, which precisely shows that there is no weight loss below 220 ºC. Hence the crystal is devoid of any physically adsorbed water on it. It is found to be the loss of 10 percent mass at 220 ºC and the remaining quantity get decomposed at 251.77 ºC. The DTA response curve also shows a sharp endothermic peak at 251.77 ºC, which indicates complete decomposition temperature. This shows very precisely that the material undergoes simultaneous melting and maximum of decomposition at the same temperature. Thus, from the thermal analysis, it is seen that D-Tartaric acid crystal decomposes with melting and is stable up to 220 ºC temperature. Therefore, the nonlinear optical single crystal can be utilized for device application till 220 ºC.

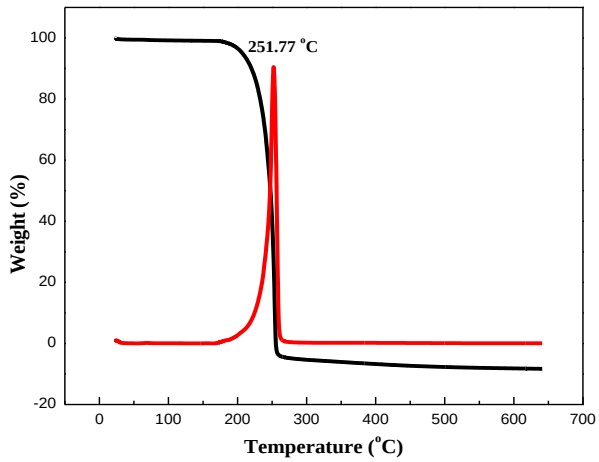

Fig. 6. TG/DTA curves of D-Tartaric acid crystal.

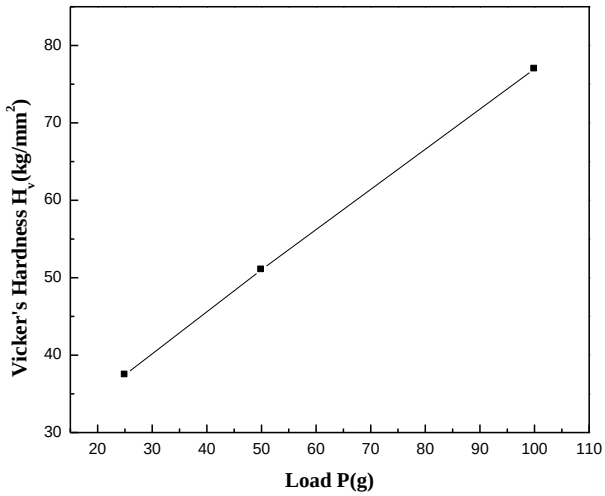

Fig. 7. Hardness Vs load graph of D-Tartaric acid crystal

The hardness graph is shown in the **Fig. 7**, from which it is observed that there is an increase of hardness with the increase of load up to 100 gram and crack develops on the crystal when 100 g load is applied. The maximum crack length developed on the crystal is 44.31 μm from the center of the indentation. Vicker's microhardness was calculated using the formula for various loads and the corresponding indentation length. The maximum hardness obtained in this material is 76.97 kg/mm^2. In order to find work hardening coefficient (n) of the grown crystal, a graph (**Fig. 8**) was drawn between logarithmic values of load and diagonal length of indentation using the Meyer's law $P = ad^n$ connecting the relationship between applied load and diagonal length of the indentation. Here, 'a' is the constant for the given material. Work hardening coefficient or Meyer index 'n' was calculated as 4.14 from the **Fig. 8**. According to Onitsch, if n lies between 1 and 1.6, the grown crystal will be a harder material and it is more than 1.6 for soft materials [**17**]. Since the calculated work hardening coefficient 'n' is more than 1.6, the grown crystal is suggested that it is a soft material. Using the formula $\sigma_y = (H_v/3)(0.1)^{n-2}$, yield

strength of the grown D-Tartaric acid single crystalline material was calculated. Where σ_y is the yield strength, H_v is the Vicker's hardness and n is the work hardening coefficient. It was calculated as 0.186 MPa from the relation and hence the grown D-Tartaric acid single crystal has low mechanical strength. The ability of a material containing a crack to resist fracture is described as fracture toughness (K_c), which is one of the most important properties of all kinds of material for any device applications. It was calculated using the formula $K_c = P/\beta C^{3/2}$, where C is the crack length from the center of the indentation, P is the applied load and β (=7) is the geometrical constant for Vickers indenter. The longest crack length developed in the grown D-Tartaric acid crystal with the applied load 100g was 44.31μm, from which the fracture toughness was calculated as 48433 kg/m$^{3/2}$. Brittleness is an important property of the crystal which determines its fracture without any appreciable deformation. It is expressed in terms of brittleness index. Using the formula $B_i = H_v/K_c$, brittleness index was calculated as 1589 m$^{-1/2}$. Elastic stiffness constant was calculated from the microhardness by Wooster's empirical relation $C_{11} = (H_v)^{7/4}$**[18]**. The maximum elastic stiffness constant for the grown D-Tartaric acid crystal is 20 x10^{12}.

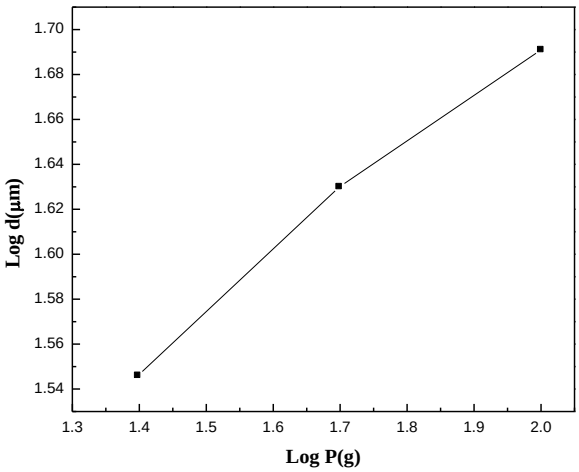

Fig. 8. Plot of log P and log d of D-Tartaric acid crystal

Conclusions

Nonlinear optical single crystal D-Tartaric acid can be grown by slow solvent evaporation technique from a saturated aqueous solution at room temperature. Various characterizations such as linear and nonlinear optics, thermal and mechanical studies were made on the grown crystals. The cell parameter and space group obtained from single crystal X-ray diffraction analysis confirms the grown crystal is D-Tartaric acid and non-centrosymmetric crystal system. The crystal possesses linear optical properties such as transmittance is more than 70% in the visible region, optical band gap is 5.1 eV and nonlinear optical property, second harmonic generation efficiency is equal to the standard potassium dihydrogen phosphate crystal. This makes the suitability of the grown crystal as a harmonic generators device in laser. Its starting melting temperature 220 ºC associated with decomposition confirms that the grown crystal can be utilized for any kind of photonic device application up to that temperature. From the microhardness studies made on the crystal, various mechanical properties were calculated, which shows that the crystal possesses low mechanical strength.

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