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Crystal Growth of Ferroelectric N,N′-Diphenylguanidinium Hydrogen (+)-L-Tartrate Monohydrate Single Crystals and Their Characterizations

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Single crystals of a new ferroelectric material, N,N′-Diphenylguanidinium hydrogen (+)-L-tartrate monohydrate (DPT), were grown from an aqueous solution using the slow evaporation solution technique (SEST). The grown DPT crystals were subjected to powder X-ray diffraction analysis and Fourier transform infrared spectral studies. The dielectric constant and dielectric loss of the crystal were determined as a function of frequency at room temperature and the results are discussed. The result shows that a DPT single crystal has some ferroelectricity with a saturated polarization of approximately 6.5 $\mu C/cm^2$ at a coercive field of about 0.5 kV/cm.

Keywords Single crystal; X-ray diffraction; dielectric properties; ferroelectric properties

Introduction

In recent years, silicon-based storage technologies could not respond to the growing demand for low power consumption storage and faster memory. In the late the 20th century, ferroelectric materials were proposed as a promising solution for highly efficient memory devices. Apart from their application in memory storage, ferroelectric devices can be used in various applications, such as sensors and actuators [1]. It is evident that materials are one of the crucial factors behind the effectiveness of ferroelectric devices. After the first discovery of ferroelectricity in Rochelle salt (potassium sodium tartrate tetrahydrate) [2] many studies have been done to search for new materials with high ferroelectricity at a temperature higher than room temperature. Recently, tartrate crystals have become a material of interest among researchers due to its remarkable physical properties, such as ferroelectricity, piezoelectricity, high permittivity, optical properties and other pertinent characteristics [3–4]. By mixing tartaric acid with an organic-based material in an aqueous solution, the grown crystal generally possesses a non-centrosymmetrical architecture. This non-symmetrical structure

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means that the crystal exhibits some remnant polarization and thus ferroelectricity when applying an external electric field [5]. On one hand, some combinations have been identified with inorganic compounds, such as NaK-tartrate and $NaNH_4$-tartrate. While, on the other hand, some combinations have been made with organic compounds, such as L-cysteine tartrate and hydroxyethylammonium L-tartrate monohydrate. N,N′-Diphenylguanidinium hydrogen (+)-L-tartrate monohydrate (DPT) has been one of the potential materials with high ferroelectricity. Paixao et al reported the structure of the DPT crystal and also presented its non-linear optical properties [6]. DPT crystallizes in an orthorhombic system have the space group of $P2_12_12_1$ and cell parameters of a = 7.099Å, b = 14.723Å, and c = 18.219Å. With a non-symmetrical structure, the DPT crystal has not only non-linear optical properties, but it may also exhibit some ferroelectricity. However, few studies have been done to investigate the ferroelectricity of DPT. Therefore, the aims of this work are to grow DPT single crystals and to characterize their properties, such as structure and ferroelectricity.

Experimental Procedure

The solvent was prepared from 1 : 1 mix of analytical grade ethanol and deionized water. Equimolar portions of N'N Diphenylguanidine and L-tartaric acid were mixed in the solvent and then stirred until they were thoroughly dissolved. The slow evaporation technique was used at room temperature to achieve a single crystal. A filter was used to protect the solution from dust and also control the evaporation rate. After the growth period of 20 days, the grown DPT crystals are shown in Fig. 1.

Characterizations

Thin slices of DPT samples were cut from the prominent face for physical characterizations. These samples were lapped and polished using a fine-grit polishing sheet with a mixture of alumina powder and ethylene glycol as the lubricant. The samples were cut and polished to have identical thicknesses. Surface defects have a strong influence on physical properties, especially the optical characteristics. In this work, we used highly polished DPT single crystals in the experiment. In this fashion, the alias from surface damage could be

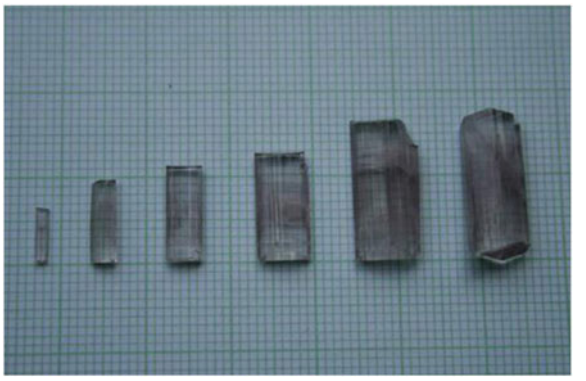

Figure 1. N,N′-diphenylguanidinium hydrogen (+)-L-tartrate monohydrate (DPT) single crystals grown using the conventional method. (Color figure available online.)

avoided, and hence, the results showed the authentic characteristics of the DPT crystals. The experiments were repeated to confirm all the data.

The lattice parameters and microstructure of the grown crystals were identified using powder X-ray diffraction (PXRD) spectroscopy and scanning electron microscopy. The functional groups of the crystals were investigated by Fourier transforms infrared spectroscopy (FTIR) spectroscopy. Dielectric measurements were performed to investigate the dielectric constant and dielectric loss of the crystals. A Sawyer-Tower circuit was operated at 273 K to measure the ferroelectricity of the DPT crystals.

Results and Discussion

X-ray Diffraction Analysis

PXRD patterns were recorded for the grown crystals at room temperature using a BRUKER powder X-ray diffractometer with $CuK\alpha$ radiation. The scanning angle was varied from 10° to 90° with a scan speed of 2°/min to study the crystallinity of the grown crystal. Finely crushed DPT powder was subjected to PXRD. The result from the PXRD spectroscopy is shown in Fig. 2. Bragg peaks are evident and well defined at the specific 2θ. This shows that the DPT samples were single crystalline with several major planes, such as (0 0 4) and (0 1 1). Since N,N′-diphenylguanidinium hydrogen (+)-L-tartrate monohydrate is an organic material, its crystal generally provides many planes to scatter the incident X-ray beam. This agrees to the PXRD spectrum which reflected the complex crystal structure with various planes.

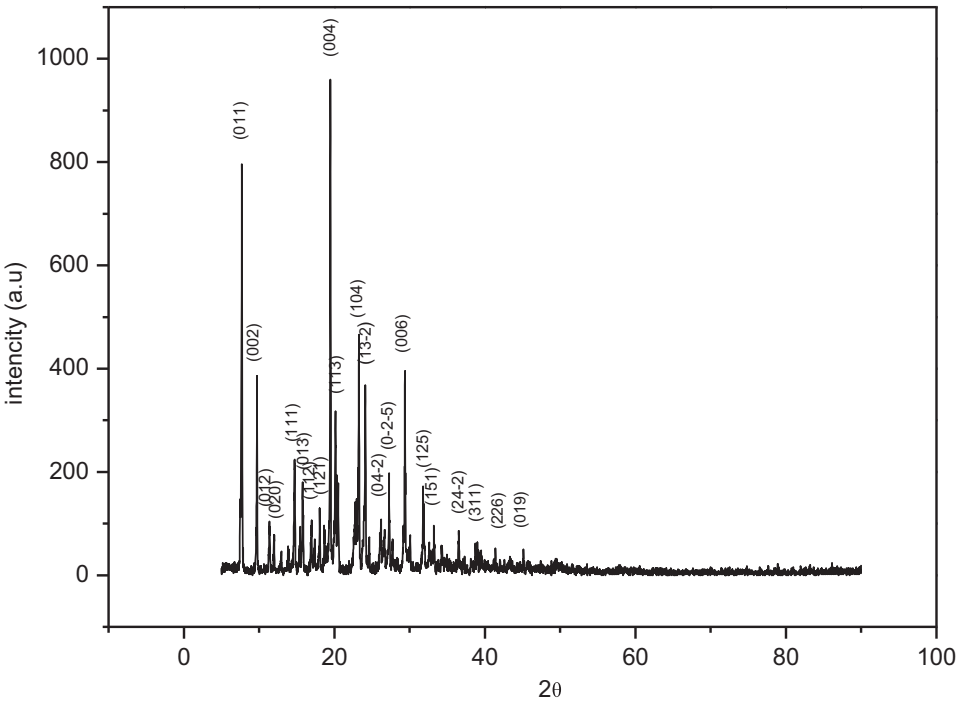

Figure 2. Powder X-ray diffraction pattern of a DPT single crystal.

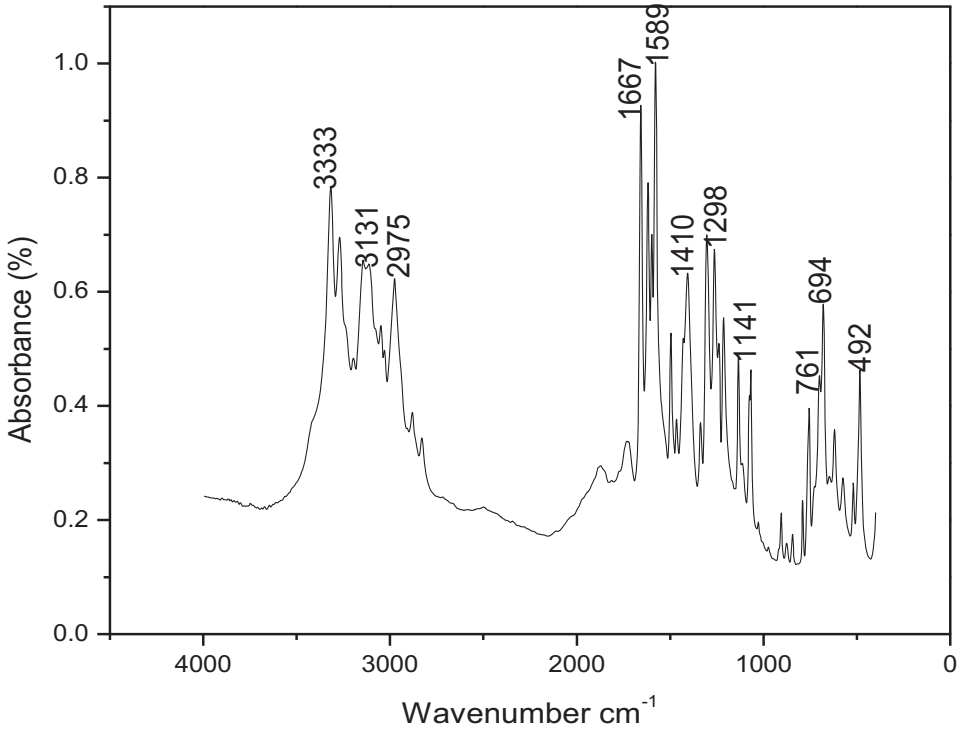

Figure 3. FTIR spectrum of a DPT single crystal.

FIIR Spectrum Analysis

A BRUKER IFS 66 V FT-IR spectrometer was used to examine functional groups in the single crystal of N,N′-Diphenylguanidinium hydrogen (+)-L-tartrate monohydrate. The absorption spectrum of the DPT is illustrated in Fig. 3. The FTIR spectrum shows a board strong peak at 3333 cm^{-1} for the O—H stretching mode of the alcohol groups in tartaric acid. The strong peaks at 3131 and 2975 cm^{-1} correspond to the absorption peak of the O—H stretching in the carbonyl groups of both diphenylalanine and tartaric acid. In addition, the spectrum shows a peak at 1667 cm^{-1} for the C=O stretching vibration of the carbonyl groups in both diphenylalanine and tartaric acid. The absorption peak of the N—H stretching in an amide group of the diphenylalanine is at 1589 cm^{-1}, while that of the C=C stretching mode of the aromatic benzene rings in diphenylalanine is at 1410 cm^{-1}. The peaks at 1298 and 1141 cm^{-1} correspond to the absorption peaks of the C-N stretching vibration in diphenylalanine. The absorption spectrum thus confirms that the grown crystal is composed of diphenylalanine and tartaric acid molecules.

Dielectric Permittivity and Loss Measurements

The DPT samples for the dielectric studies were prepared in the form of thin plates of approximately 1 mm thickness. The prepared samples were transparent and free from the large noticeable defect. The DPT crystal was coated with silver layers on both sides. The dielectric permittivity (ε_r) was determined at room temperatures with a frequency range of 100 Hz to 1 MHz using a Hewlett Packard 4194 Impedance/Gain phase analyzer.

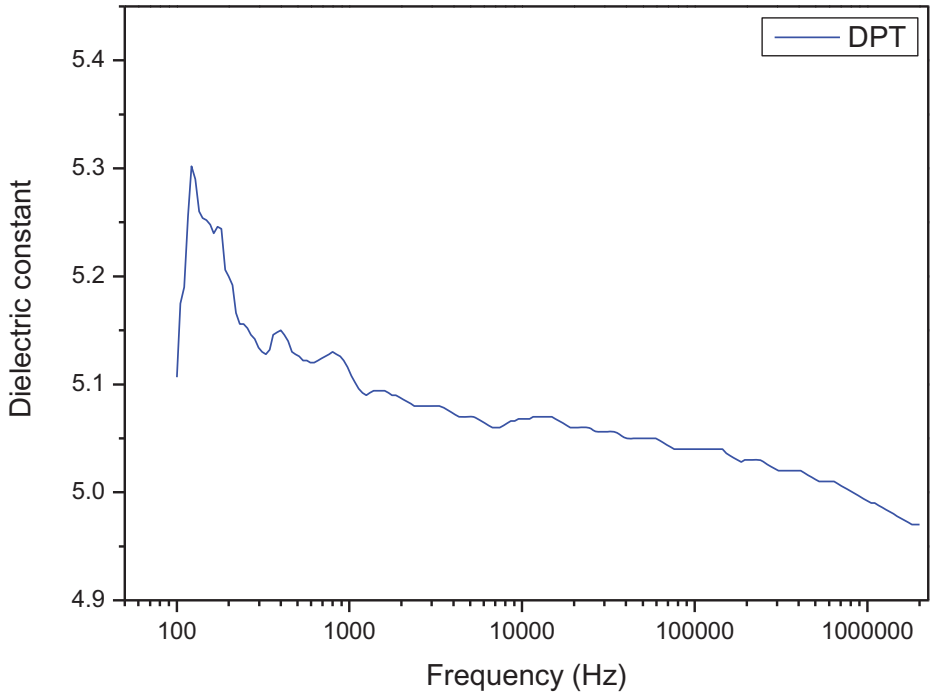

Figure 4. Frequency dependent dielectric constant of a DPT single crystal. (Color figure available online.)

The samples coated with silver were then placed between two copper electrodes to form a parallel-plate capacitor. The variation of the dielectric constant of the DPT crystal with frequency is shown in Fig. 4. The maximum dielectric constant of the grown DPT crystal is about 5.4 at 100 Hz. When the frequency is increased, the dielectric permittivity decreases significantly.

The frequency dependence dielectric loss of the DPT crystal is shown in Fig. 5. At lower frequency, the dielectric loss has a high value of 0.07 at 1 MHz and it decreases to 0.01 at 100 Hz in the case of higher frequency. The characteristic of a low dielectric loss at a high frequency for the DPT crystal suggests that the sample possesses enhanced optical quality with few defects, and hence this parameter is of vital importance for various practical ferroelectric applications. The dielectric loss in the crystal is due to domain relaxation, solvent inclusions during growth and dislocations/strain centers which pin the domains.

Ferroelectric P-E Hysteresis Loop Analysis

To investigate the ferroelectric properties a Sawyer-Tower circuit [7], using a RT66A ferroelectric test system, was operated at 273 K to measure the ferroelectric hysteresis of the crystals. DPT samples were cut from the dominant face for PE hysteresis loop. The samples were polished to get a smooth surface. The cut and polished DPT wafers were shaped to the thickness of 1 mm and equipped with 3×3 mm^2 gold electrodes. Ferroelectricity of the DPT was measured using a Sawyer-Tower circuit with an applied electric field of about 1 kV/cm (Radiant Technology Incorporation-Precision Work Station). The electric field was limited below 1 kV/cm to prevent any damage to the DPT crystal.

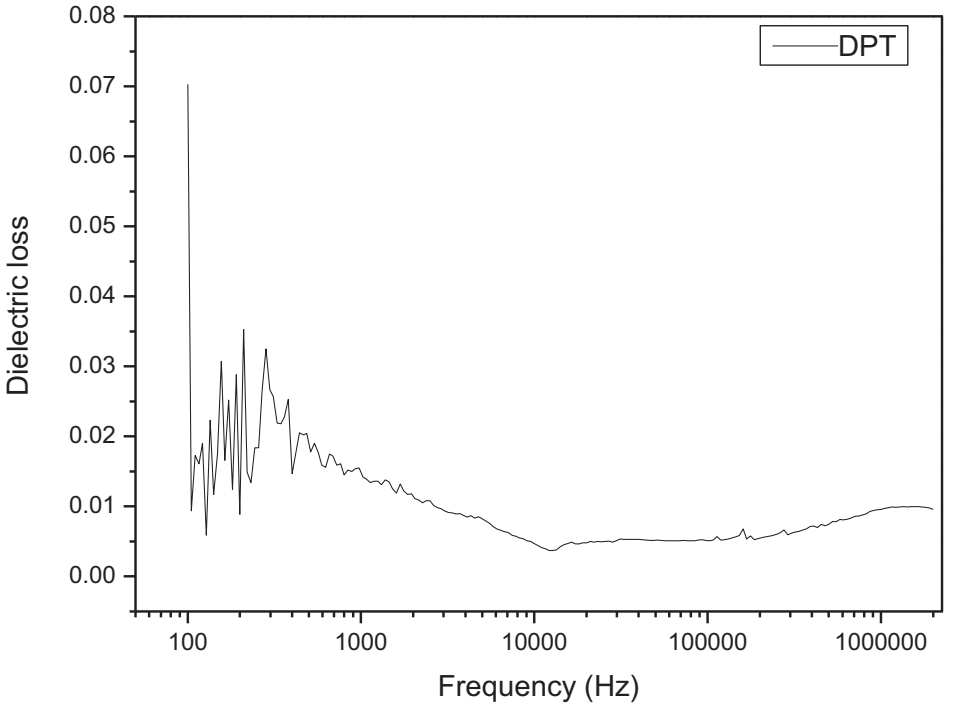

Figure 5. Frequency dependent dielectric loss of a DPT single crystal.

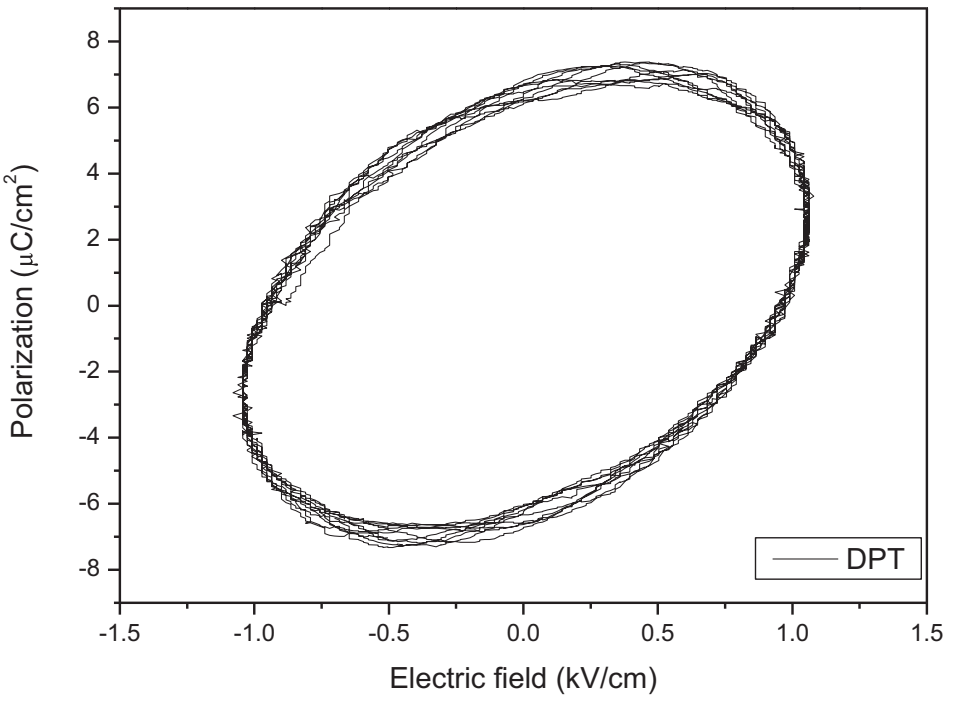

Figure 6. PE Hysteresis loop analysis of a DPT single crystal.

The result shows that the P-E hysteresis loop of the DPT crystal is obvious and board as shown in Fig. 6. Saturation polarization can be observed at about 0.5 kV/cm. Without the external electric field (E = 0 V/cm), the remnant polarization is approximately 6.5 μC/cm^2. From this result, it is evident that DPT crystals possess some ferroelectricity. However, its ferroelectricity is weak and needs further studies for improvement. Therefore, some further studies are required to examine the Curie temperature (Tc) of the DPT crystal, and hence, its ferroelectric property can then be experiment at the appropriate temperature.

Conclusions

Optically transparent DPT crystals of length 18 mm and diameter 8 mm were grown in a period of 20 days using the slow evaporation solution technique (SEST). The average growth rate achieved was 1 mm/day. The crystal structure was confirmed by PXRD analysis and FTIR spectrum analysis. Its dielectric constant is frequency-dependent and inversely proportional to the frequency. P-E hysteresis studies in a SEST grown DPT crystal showed a well saturated circular hysteresis loop and the observed remnant polarization is 6.5 μC/cm^2 with a coercive field of 0.5 kV/cm. Despite the ferroelectric results at 273 K, SEST may be a promising method to grow a DPT crystal with some ferroelectricity.

Acknowledgments

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