Synthesis, theoretical and electrical properties of L-phenylalaninium trichloroacetate hemihydrate (PACAH) single crystals

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Semi-organic single crystal of L-Phenylalaninium Trichloroacetate Hemihydrate (PACAH) has been grown from aqueous solution. The grown crystals were characterized by single crystal XRD analysis. Some fundamental data such as valance electron, plasma energy, Penn gap, Fermi energy and electronic polarizability of PACAH crystal is reported. The dielectric constant of the grown crystal has also been studied as a function of frequency at various temperatures. The photoconductivity reveals the negative nature of the photocurrent in these crystals. Ferroelectric property of the grown crystal has been confirmed by hysteresis loop studies.

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1. Introduction

Ferroelectric crystals are a special case of crystals that exhibit a spontaneous polarization over some range of temperature. This polarization can be reversed or reoriented by the application of an external electric field. Ferroelectric materials have attracted much attention, especially because of their applications in non-volatile memory devices [1,2]. Triglycine sulfate (TGS) is a well-known ferroelectric crystal finding many applications in IR detectors and laser devices [3]. Doped organic – inorganic ferroelectric compounds on the basis of Triglycine sulfate (TGS) continue to be important materials used in the fabrication of high sensitivity infrared detectors and also for construction of vidicons operating at room temperature [4]. L-Phenylalaninium Trichloroacetate Hemihydrate (PACAH) is identified as a new ferroelectric crystal. PACAH which crystallizes in noncentrosymmetric space group C2 has been reported previously [5-6]. In the present study, growth of semi-organic material, PACAH has been carried out by slow evaporation method at room temperature and some physical parameters such as valance electron plasma energy, Penn gap, Fermi energy and electronic polarizability have been obtained for PACAH single crystal. The dielectric constant has been determined as a function of frequency at various temperatures for the PACAH single crystal. In addition, ferroelectric property of the grown crystal has been confirmed by hysteresis loop studies.

2. Crystal growth

L-Phenylalanine and trichloroacetic acid (AR grade) were dissolved in millipore water (18.2 MΩ cm^{-1}) in mole ratio of 1:1 at room temperature. The prepared solution was stirred well for 3 hours using a magnetic stirrer to avoid coprecipitation of the material and clear solution was obtained. The solution was taken in a covered container for controlled evaporation and kept at room temperature. After 10 days the PACAH material was crystallized at the bottom of the container. The synthesized material was purified by repeated recrystallization process and used for the growth of crystals. Good-quality transparent PACAH single crystals of size 16 x 4 x 2 mm^3 have been obtained in 20 days and are shown in Fig. 1.

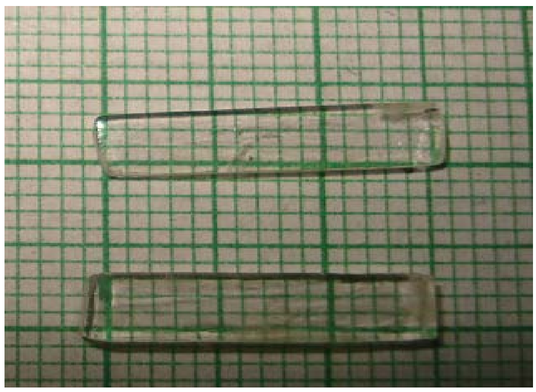

Fig. 1. As grown crystal of PACAH.

3. Results and discussion

Density of PACAH Crystal

The density of PACAH crystal was calculated using the equation [7]

$$\rho = MZ / NAabc \tag{1}$$

Where M is molecular weight of PACAH, molecular unit cell Z = 8, NA is Avogadro's number and a, b and c are the lattice parameters of PACAH crystal. The theoretical density is found to be 1.38 g/cm^3. The density of PACAH crystal was measured experimentally by the floatation method at room temperature (32ºC), and the measured density can be obtained using the expression

$$\rho = M\,\rho_{solvent} / m - m' \tag{2}$$

where m is the mass of PACAH crystal sample in the air, m′ is the mass when the PACAH crystal sample was immersed in CCl_4 and $\rho_{solvent}$ is the density of solvent (CCl4) used at measured temperature. The density was measured by floatation technique. From this measurement, the density of the crystal is found to be 1.376 g/cm^3, which is in good agreement with the theoretically found value.

3.1 Single crystal X-ray diffraction and fundamental parameters

The single crystal XRD data of the grown PACAH crystal was obtained using ENRAF NONIUS FR 590 single crystal X-ray diffractometer. From the single crystal X-ray diffraction data, it was confirmed that the unit cell dimensions are a = 19.78 Å, b = 6.16 Å, c = 26.66 Å, β = 109.52°, V = 3060 Å^3 and it belongs to monoclinic system with space group C2. The lattice parameters derived are in good agreement with the reported values confirming the identity of the grown crystal [5]. The molecular weight of the grown crystal is M=338 g, and total number of valence electron Z=110**.** The density of the grown crystal was found to be ρ=1.38 g cm^{-3} and dielectric constant at 1 MHz is ε_∞ =72. The valence electron plasma energy, $\hbar\omega_P$ is given by

$$\hbar\omega_P = 28.8\left(\frac{Z\rho}{M}\right)^{\frac{1}{2}} \tag{3}$$

where Z is the total number of valence electrons, ρ is the density and M is the molecular weight of the PACAH single crystal. The Plasma energy is terms of Penn gap and Fermi energy [8] in eV is given as

$$E_P = \frac{\hbar\omega_P}{\left(\varepsilon_\infty - 1\right)^{1/2}} \tag{4}$$

and

$$E_{\mathrm{F}} = 0.2948\left(\hbar\omega_P\right)^{4/3} \tag{5}$$

Polarizability, α is obtained using the relation [9]

$$\alpha = \left[\frac{\left(\hbar\omega_P\right)^2 S_0}{\left(\hbar\omega_P\right)^2 S_0 + 3E_P^2}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24}\,cm^{-1}$$

where S_0 is a constant for a particular material, and is given by

$$S_0 = 1 - \left[\frac{E_F}{4E_F}\right] + \frac{1}{3}\left[\frac{E_F}{4E_F}\right]^2 \tag{7}$$

The value of α so obtained agrees well with that of Clausius-Mossotti equation, which is given by,

$$\alpha = \frac{3M}{4\rho\pi N_a}\left(\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2}\right) \tag{8}$$

where the symbols have their usual significance. N_a is Avagadro number and the calculated fundamental data on the grown crystal of PACAH are listed in Table 1.

Table 1. Some theoretical data for PACAH single crystal.

Parameters	Values
Plasma energy (eV)	19.30
Penn gab (eV)	2.29
Fermi gap (eV)	15.26
Polarizability (cm^3) from Penn analysis	9.15×10^{-23}
Polarizability (cm^3) from Clausius - Mossotti Equation	9.32×10^{-23}

3.2 Dielectric studies

The solution grown single crystals of PACAH of thickness of 1 mm and 68 mm^2 area is used for dielectric studies. The dielectric constant of PACAH single crystals are measured with the help of impedance analyzer and further automated by using a computer for data recording, storage and analysis. The dielectric constant is calculated using the formula $\varepsilon' = Ct / \varepsilon_0 A$, where C is the capacitance (F), t the thickness (m), A the cross-sectional area (m^2) of the sample and ε_0 is the absolute permittivity of the free space having a value of 8.854×10^{-12} Fm^{-1}.

A dielectric characteristic study of the solution grown PACAH indicates its response to an applied electric field. Variations in the dielectric constant (ε$'$) may be attributed to different types of polarizations, which may come into play at different stages of its responses to varying temperature and frequency of the applied alternating field.

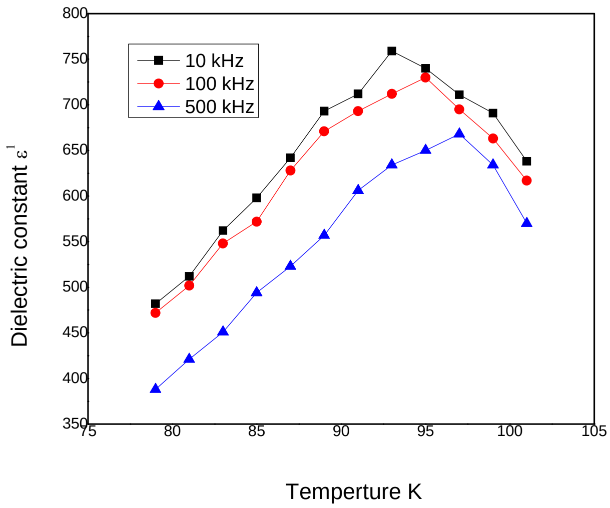

Fig. 2. Plot of dielectric constant ε/ against temperature at different frequencies.

The variation of dielectric constant with temperature at different frequencies of the applied ac field for PACAH single crystals is shown in Fig. 2. The dielectric constant increases with the rise in temperature upto its maximum value (ε_{max}) at the Curie temperature (T_c) and then decreases with further increase in temperature. It is observed that the compound undergo a phase transition from ferroelectric to paraelectric at a particular temperature. Curie temperature T_c shifts towards higher temperature side at higher frequencies. It is observed that material has the maximum value of the dielectric constant at a particular temperature for all the three frequencies (10, 50 and 100 kHz) which indicates the existence of diffuse phase transition. So it is called a "relaxor" ferroelectric material because of its dispersive (frequency dependent) dielectric response and diffuse phase transition around the Curie point T_c. They are attractive in applications such as medical imaging, telecommunication and ultrasonic devices.

3.3 Photoconductivity studies

The photoconductivity studies of grown crystals were carried out by connecting the sample in series with a dc powder supply and a Pico ammeter (Keithley 480) at room temperature. The applied field was increased from 500 to 1900 V/cm, and the corresponding dark current and photocurrent were recorded. Fig. 3 shows the dependence of the dark current and photocurrent with respect to the applied field at room temperature. The dark current and photocurrent increase linearly with respect to the applied field. At every instant, the dark current is greater than the photocurrent, which is called negative photoconductivity. This may be attributed due to decrease in either the number of free charge carriers or their lifetime when subjected to radiation.

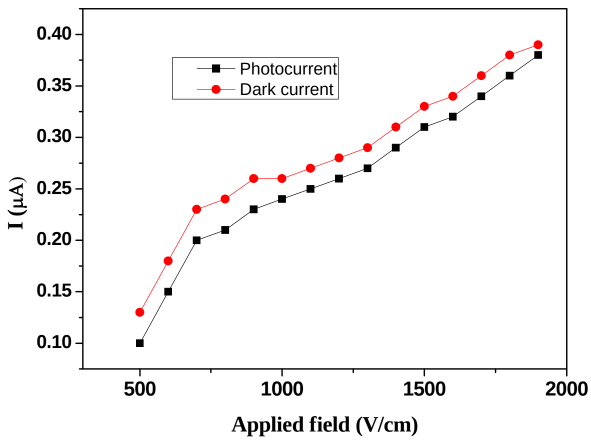

Fig. 4. Dark current and photocurrent as a function of applied field.

3.4 Hysteresis loop studies

Registration of hysteresis loop is a standard technique for the fast characterization of ferroelectric crystals [10]. The fundamental ferroelectric P-E hysteresis traced using computer interface Sawer – Tower Circuit [11] for PACAH crystals at the frequency of 50 Hz at room temperature is shown in Fig. 4. In order to examine the P-E Hysteresis loop, the grown sample is cut from grown crystals by a wet thread saw followed by polishing. The crystals are investigated having an electrode area of 27 mm^2 and a thickness of 1.52 mm. Gold electrodes are deposited on the polished surface. The measured coercive field (E_c) is 3.8 kV/cm. The positive polarization (P_s) parameter state saturates at a value of 0.3 $\mu C/cm^2$. It reveals that this material can be used for the fabrication of non-volatile memory devices and IR detectors.

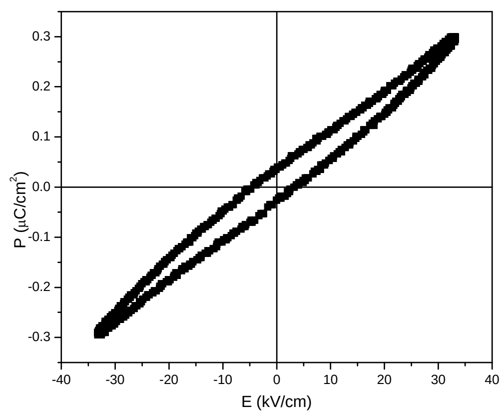

Fig. 4. P-E Hysteresis loop of PACAH crystal.

4. Conclusions

Good optical quality single crystal of PACAH was grown by using the slow evaporation technique. The lattice parameters were calculated by single crystal X-ray diffraction and it was confirmed that the crystals belong to the monoclinic system with the space group C2. The physical parameters such as valence electron plasma energy, Penn gap, Fermi energy and electronic polarisability have been determined for the PACAH crystal. The variation of dielectric constant was studied at various temperatures. Photoconductivity studies confirm that the crystal possesses a negative photoconductivity. Ferroelectric property of the crystal has been identified by hysteresis loop studies. Thus, PACAH crystal can be used for the fabrication of non-volatile memory devices and IR detectors.

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