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Synthesis, growth and characterization of L-prolinium trichloroacetate single crystal for nonlinear optical applications

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Single crystals of an organic nonlinear optical material, L-prolinium trichloroacetate has been synthesized and bulk crystals have been grown by slow cooling method. The grown crystals were characterized by single crystal X-ray diffraction, fourier transform infrared spectroscopy, thermal and electrical studies. Nonlinear optical study confirms the suitabilities of the as grown crystals for the nonlinear optical applications.

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Keywords: Crystal Growth, Crystal structure, Dielectrics, Non-linear applications

1. Introduction

Extensive studies have been made on the synthesis and crystal growth of nonlinear optical (NLO) materials over the past decade because of their potential applications in the field of telecommunications, optical signal processing and optical switching. Organic nonlinear optical materials are attracting a great deal of attention due to their potentially high nonlinearities and rapid response in the electrooptic effect compared to inorganic NLO materials. In search for new organic NLO materials, aromatic compounds with donor and acceptor substituents are extensively studied. A number of crystals with large nonlinear coefficients have been reported. However, this kind of materials is seldom useful in the ultraviolet (UV) region, because the distance between energy levels in conjugated Π bonds gets smaller due to the strong conjugation effect. In solid state, amino acid contains the donor and acceptor groups, which provide the ground state charge asymmetry of the molecule, required for second – order nonlinearity [1-6]. Proline is an abundant amino acid in collagen and is exceptional among the amino acids because it is the only one in which the amine group is part of a pyrrolidine ring, making it rigid and directional in biological systems [7]. L-proline has been exploited for the formation of salts with different organic and inorganic acids [8]. Recently, several salts of proline were reported such as L-prolinium tartrate, L-prolinium picrate [9-10]. In this present communication, we report the synthesis and growth of L-prolinium trichloroacetate (LPTC), with chemical formula L-pro. CCl_3COOH. The grown crystals were characterized by single crystal X-ray diffraction, FTIR, thermal, electrical and NLO studies.

2. Experimental

2.1 Synthesis and purification of LPTC

LPTC was synthesized by the reaction between L-proline and trichloroacetic acid taken in the stoichiometric ratio of 1:1. The calculated amount of trichloroacetic acid was first dissolved in millipore water. L-proline was then slowly added to the solution and stirred well using a temperature controlled magnetic stirrer to yield a homogeneous mixture of solution. Then the solution was allowed to evaporate at room temperature, which yielded the crystalline salt of LPTC. The purity of the synthesized salt was improved by successive recrystallization process.

2.2 Crystal growth of LPTC

The starting material of LPTC was dissolved in millipore water. The saturated solution of LPTC was prepared at 40°C and the solution was filtered to remove any impurities. Good optical quality seed crystals obtained by slow evaporation method were used for the bulk growth. The growth was carried out in a constant temperature bath of controlling accuracy ± 0.01 °C. A cooling rate of 0.2 °C/day was employed during the initial and final stages of the growth period. Optical quality crystal of LPTC has been grown over a typical growth period of 15 days. As grown single crystal of LPTC is shown in Fig. 1.

3. Results and discussion

3.1 Single crystal X-ray diffraction analysis

The grown crystals were subjected to single crystal X-ray diffraction analysis using ENRAF NONIUS CAD-4 X-ray diffractometer with MoKα (λ = 0.71069 Å)

radiation. This study reveals that the grown crystal belongs to trigonal system with the space group $P3_1$ and Z = 3. The lattice parameter values are a = b = 9.810 (3) Å, C = 10.118 (5) Å, α = β = 90°, γ = 119.94 (2)° and volume = 844.5 (1) $Å^3$, which is in good agreement with the reported value [11]. Fig. 2 shows molecular structure of LPTC crystal. The proline molecule exists in the cationic form, with a positively charged amino group and a neutral carboxylic acid group. The trichloroacetic acid is in the anionic state.

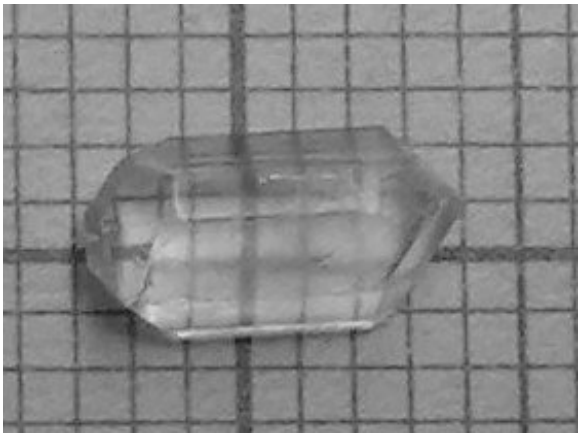

Fig. 1. As grown LPTC single crystal from aqueous solution pH of 2.0.

3.2 FTIR analysis

The FTIR spectrum of LPTC crystal was recorded in the range 400 – 4000 cm^{-1} using Bruker IFS 66V by KBr pellet technique. Fig. 3 shows the FTIR spectrum of LPTC crystal. The peak at 3151 cm^{-1} is due to N-H vibration. The C = O stretching mode give a peak at 1732 cm^{-1}. The asymmetric and symmetric vibrations of COO^- occur at 1645 and 1401 cm^{-1} respectively. The peaks at 1572 and 678 cm^{-1} are assigned to NH_2^+ and COO^- scissoring. The C-H bending mode occur at 1364 cm^{-1}. The twisting, wagging and rocking of CH_2 are observed at 1329, 1227 and 824 cm^{-1}. The C-C and C-C-N stretching modes give a peak at 929 cm^{-1}. The peak at 747 cm^{-1} is assigned to skeletal deformation of pyrrolidine ring. The other peaks at 605 and 469 cm^{-1} are assigned to wagging and rocking of COO^- and on comparison of the spectra with L-proline illustrates the shift in peak position as well as the change in the intensity of the peak below 1750 cm^{-1}. It is evident that the spectrum is different from that of pure L-proline and hence L-proline interacts with trichloroacetic acid, which also has support from the XRD analysis.

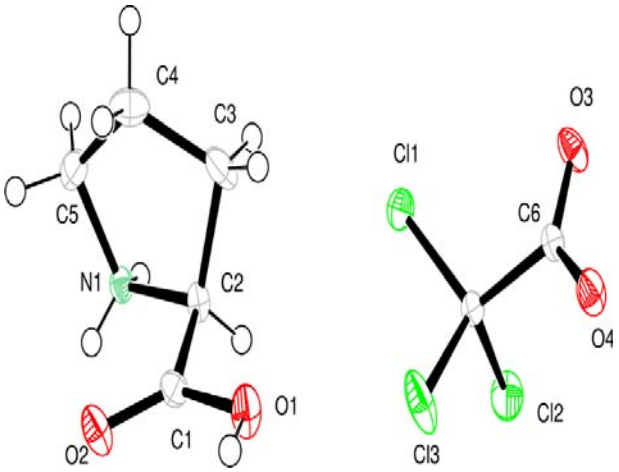

Fig. 2. The molecular structure of LPTC crystal, with the atom-numbering scheme (50% probability).

3.3 Thermal analysis

Thermogravimetric analysis (TGA), Differential thermal analysis (DTA) and differential scanning calorimetry (DSC) of LPTC crystals were carried out simultaneously in the temperature range 30 to 900°C in the nitrogen atmosphere at a heating rate of 20°C/min using TA instrument SDT Q600. The TGA, DTA and DSC curves of LPTC are shown in Fig. 4a and Fig. 4b. From the TGA curve, it is observed that the compound starts to lose single molecule of amino group at about 114°C and continues upto 131°C. A second dissociation occurred between 195 - 263°C due to evolution of carbon dioxide. The percentage of residue obtained at 888°C is equal to 15.84. In the DTA curve, the endothermic peak at 127.5°C corresponds to melting point of the substance and then it undergoes an endothermic peak at 231°C, which is associated with weight loss as observed from the TGA curve. From the DSC curve, the crystal of LPTC was stable upto its melting point 127.1°C.

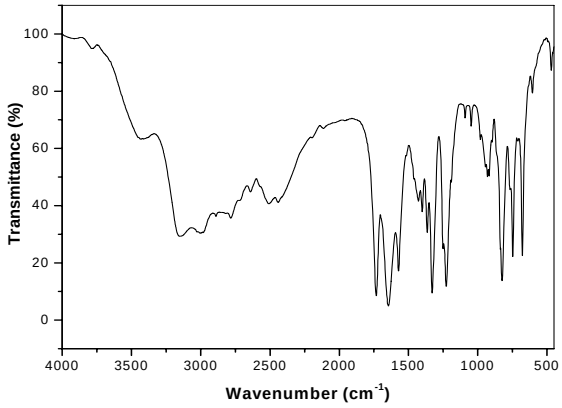

Fig. 3. FTIR spectrum of LPTC.

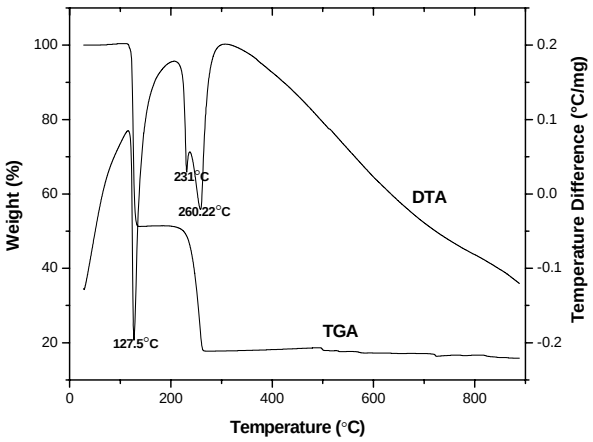

Fig. 4a. TGA and DTA curves of LPTC.

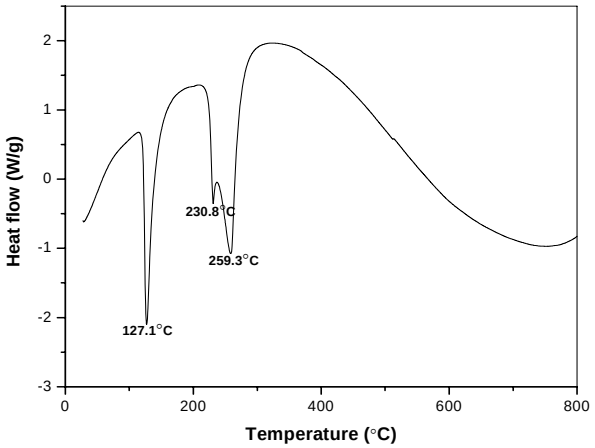

Fig. 4b. DSC curve of LPTC.

3.4 Dielectric studies

The dielectric constant and the dielectric loss of the LPTC crystal were measured at different temperatures using HIOKI 3532-50 LCR HITESTER in the frequency region 100 Hz to 5 MHz. Each sample was electroded on either side with silver paste with air drying to make it behave like a parallel plate capacitor. The dielectric constant (ε') is higher at the lower frequencies and then decreases with the increasing frequencies and saturates and the dielectric loss (ε'') decreases with increasing frequency for LPTC crystals (Fig. 5a and 5b). The large value of dielectric constant at low frequency is due to the presence of space charge polarization. When the electric charge carriers cannot follow the alternation of the a.c electric field applied beyond a certain critical frequency [12], the dielectric constant decreases with increasing frequency and remains constant. Further the dielectric constant increases with the increasing temperature. The hopping (exchange) of the charge carriers in the lattice sites (which is responsible for electrical conduction) is thermally activated by increasing temperature. As a result, the dielectric polarization increases, causing an increase in ε' and ε''. The characteristic of low dielectric constant and dielectric loss with high frequency suggests that the sample possesses enhanced optical quality with lesser defects and this parameter is of vital importance for NLO applications.

3.5 NLO studies

The NLO property of LPTC crystal was initially studied by Kurtz and Perry powder technique [13]. The sample was illuminated using Spectra Physics Quanta-ray Nd: YAG laser with the first harmonic output of 1064 nm with pulse width of 8 ns. The second harmonic signal generated in the crystal was confirmed from the emission of green radiation of wavelength 532 nm.

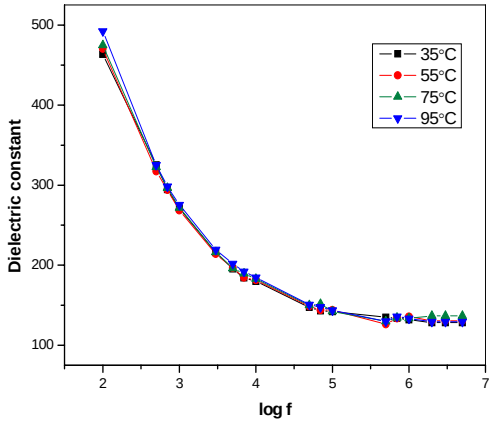

Fig. 5a. Variation of dielectric constant as a function of frequency.

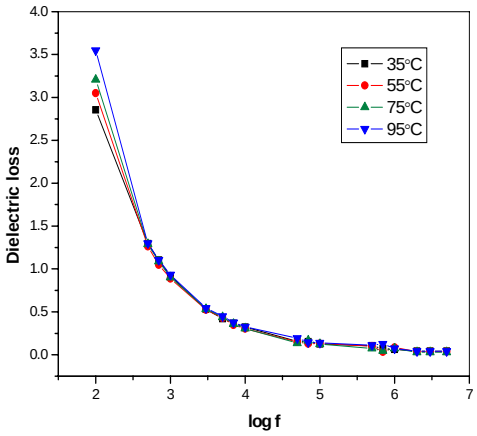

Fig. 5b. Variation of dielectric loss as a function of frequency.

4. Conclusion

The bulk single crystals of L-prolinium trichloroacetate were grown by slow cooling method. The

single crystal XRD analysis revealed that the LPTC crystal belongs to trigonal system. FTIR spectrum confirmed the functional groups present in the grown crystal. Thermal analysis indicates that the crystal has good thermal stability. DSC analysis revealed that LPTC is thermally stable upto 127.1 ^{o}C . The dielectric studies shows that the low dielectric constant and dielectric loss of the crystal at high frequency region. The second harmonic generation property was confirmed by Kurtz Perry powder technique. Thus L-prolinium trichloroacetate is a promising material for nonlinear optical applications.

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