Arabian Journal of Chemistry (2016) xxx, xxx–xxx

King Saud University

Arabian Journal of Chemistry

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ORIGINAL ARTICLE

In-depth behavioral study of l-Prolinium Trichloroacetate single crystal: An efficient candidate for NLO applications

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Received 21 June 2016; accepted 15 September 2016

KEYWORDS

X-ray diffraction;
Crystal growth;
Photoluminescence;
Thermal conductivity;
Specific heat;
Thermal diffusivity

Abstract Organic compounds have constantly proved to be a proficient candidate for nonlinear optical (NLO) applications. In this respect an organic amino acid compound i.e. l-Prolinium Trichloroacetate single crystal has been synthesized and grown through slow evaporation solution growth technique. The lattice parameters obtained from single crystal X-ray diffraction were comparable with reported one. The diffraction pattern along the strain present inside the crystal was measured through powder X-ray diffraction technique. Its photoconductivity has also been observed, in which the traits of dark and photon current were recorded over a range of applied voltage. Further, birefringence was performed for the sample in which it was found that the crystal is having negative optical homogeneity character. The thermal transport parameters were calculated through photo-pyroelectric technique. Its resistance toward the laser beam was examined using

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Peer review under responsibility of King Saud University.

Production and hosting by Elsevier

http://dx.doi.org/10.1016/j.arabjc.2016.09.011

Please cite this article in press as: Thukral, K. et al., In-depth behavioral study of l-Prolinium Trichloroacetate single crystal: An efficient candidate for NLO applications. Arabian Journal of Chemistry (2016), http://dx.doi.org/10.1016/j.arabjc.2016.09.011

laser damage threshold technique. The mechanical characteristics of the single crystal were determined on nanoscale using Oliver–Pharr method.

1. Introduction

Amino acid based organic compounds have shown excellence in various applications of nonlinear optics. The reason for such behavior is the presence of asymmetry in structure and the high order of conjugated molecules. There are many factors on which selection of materials depends i.e. optical properties, physical and thermal stability, etc. which can be further used for device fabrication like scintillation detector, laser, electric-optic modulator and many more. Amino acids contain zwitter ion i.e. —COOH (electron donor) and —NH_2 (electron acceptor), that are connected through strong hydrogen bonding which is responsible for its structural as well as physical characteristics (Nagaraja et al., 1998; Suresh Kumar et al., 2006, 2012; Srinivasan et al., 2006; Vijayan et al., 2006; Xu, 1983; Chemla and Zyss (Eds.), 1987).

Widely, there are three categories of nonlinear optical materials: organic, semi-organic, inorganic materials. Among all these organic materials are found to be the most promising candidate because the molecules in these compounds are connected through weak Vander-Waals forces. Apart from the interaction, the compound should be non-centrosymmetric in structure which is key aspect for second harmonic nonlinear optical applications. It was proved that the amino acids contain all the components that are accountable for NLO responses. In this respect, many new amino acid based single crystals have grown to fulfill the requirements. There are various examples of amino acids based compound that shows the higher order SHG efficiency such as L-Arginine Phosphate (3 times of KDP) (Yokotani et al., 1989), L-Threonine Picrate (43 times of KDP) (Natarajan et al., 2010), L-Asparagine Picrate (66 times than KDP) (Srinivasan et al., 2006) and many more. Also, there are various organic compounds other than amino acids that can show the characteristics of NLO behavior such as azobenzene and pseudostilbenes (Jerca et al., 2013; Nicolescu et al., 2010). Mostly these compounds exist in the form of polymer thin films and are centrosymmetric in structure (Jerca et al., 2013). Its synthesis process requires lot of reagents which was quite tedious and performed in controlled environment whereas in single crystals the synthesis process is simple and cost efficient. As it is known that single crystals are in most stable state among solids, there has been no deterioration or masking of the properties of the compound in the form of single crystal. Therefore, amino based compound single crystals have more reasonable possibility for NLO applications.

The unit cell dimensions of L-Proline Monohydrate single crystal were initially reported by Sasisekharan (1959). The detailed information of its crystal structure was given by Janczak and Luger (1997) in which it was mentioned that the compound contains pyrrolidine ring which leads to interruption in α-helix. The structure of L-Proline confirmed that there is a presence of Zwitter ion form which proves that it could be an efficient nominee for nonlinear applications. There are series of L-Proline based compounds such as L-Prolinium Tartrate (Thukral et al., 2014), Bis(L-Proline) Nitrate (Selvaraju and Kirubavathi, 2013), L-Prolinium Phosphite (Fleck et al., 2015), L-Prolinium Picrate (Martin Britto Dhas et al., 2008), and L-Prolinium Thiourea (Umamaheswari et al., 2014).

In the title compound i.e. L-Prolinium Trichloroacetate (LPTCA), Proline acts as a cation and Trichloroacetate acts as an anion. Mostly Trichloroacetic acid crystallizes with amino acids and amides. The cation and anion are coupled with each other through hydrogen bonding by N—H···O and O—H···O. In the first report of L-Prolinium Trichloroacetate single crystal by Rajagopal et al. (2003), it was found that the compound belongs to trigonal crystal system which is very uncommon among amino acids.

2. Material and methods

2.1. Salt preparation and growth of single crystal

Before growth procedure it was necessary to synthesize the salt of the desired compound. For that initial step was to take the raw materials in a definite ratio. The measured solute was finely dissolved in an appropriate solvent to make a solution. In the present case, commercially available L-Proline and Trichloroacetic acid were taken in an equimolar ratio. They were dissolved in double distilled water and were stirred for next 4–6 h to form a solution. This solution was further dried to synthesize the salt. To purify the extracted salt, repeated practice of re-crystallization has been performed. The obtained purified salt was used to make saturated solution and was kept in constant temperature bath at 35 °C. After 35 days a fully transparent crystal was achieved from mother solution as shown in Fig. 1 of dimensions $5 \times 3 \times 2\ mm^3$.

3. Result and discussion

3.1. Single crystal X-ray diffraction

For the proper verification regarding the formation of compound, single crystal X-ray diffraction technique was carried out. This technique gives the information about lattice

Figure 1 Harvested single crystal from mother solution of L-Prolinium Trichloroacetate single crystal.

parameters, crystal system, space group, atom location, bond types, bond locations, bond angles, and chemical content of unit cell. The grown specimen was subjected to single crystal XRD using Bruker APEX CCD diffractometer. Mo Kα radiation of wavelength (λ = 0.71073 Å) has been taken as source for single crystal XRD. From the performed experiment, the obtained results reveal that the crystal belongs to trigonal system and its lattice parameters i.e. $a = b$ = 9.8433 Å, c = 10.1145 Å were correctly matched with the reported one (Rajagopal et al., 2003; Boopathi et al., 2012).

3.2. Powder X-ray diffraction

In powder X-ray diffraction (PXRD), a good quality single crystal was crushed into fine powder to find out the diffraction pattern of formed compound using Bragg's equation i.e. $\lambda = 2d\sin\theta$ where λ is incident wavelength, d was spacing between planes and θ was the diffraction angle. The sample has been scanned over a range of 2θ i.e. 10–80 arc sec, to attain diffraction planes. L-Prolinium Trichloroacetate (LPTCA) single crystal was crushed in the form of fine powder which was subjected to Rigaku X-ray diffractometer using Cu Kα as source to produce incident radiation ($\lambda \sim 1.54$ Å) with scan speed of 4°/min. A plot between intensity and 2θ was drawn, as shown in Fig. 2(a). The strain present in lattices of crystal was calculated by Hall Williamson equation i.e. $\beta\cos\theta = K\lambda/\tau + \eta \sin\theta$, where β, θ, K, λ and τ are full widths at half maxima (FWHM) of diffraction peak, Bragg diffraction angle of the peak, Scherrer constant, wavelength of X-rays and crystallite size respectively. The motive of measuring strain was to get information regarding the presence of defects/deformities inside the vicinity of crystal. There are mainly two key aspects on which strain depends: XRD peak location and XRD peak width. From the calculated data, graph has been drafted between $\beta\cos\theta$ and $\sin\theta$ as shown in Fig. 2(b). The value of strain for LPTCA single crystal was obtained as 0.0067 with a minor error of 0.00152 from the slope of the curve.

3.3. Photoconductivity

Photoconductivity is a non-destructive technique, which is used to measure conductivity of crystal in the presence and absence (dark conductivity) of light. Photoconductive materials have tendency to transform low energy input pulses into electric signals. These materials can be used as photo resistors, photo detector and in many more devices. LPTCA single crystal of 3 mm was polished and coated by silver paste to form electrode on both sides. The sample was placed onto a microscopic slide and connected with DC power supply in series and KEITHLEY 485 picoammeter. Voltage over the range of 10–100 V was applied to the sample. Both dark and photo current can be observed using this instrumental arrangement. The plot of Dark and photon current with respect to applied voltage is shown in Fig. 3.

From the figure it is clear that photo current lags behind dark current over all the range of applied voltages. This type of feature interprets that the title compound belongs to negative photoconductivity. Usually such behavior occurs when there is shortage of charge carrier during the illumination of sample as compared to its original (dark) state. Because when the light falls on the sample its charge carriers (i.e. electrons) get excited and shift to higher energy state, which in turn **results** in the formation of vacancy. These formed vacancies (holes) are left for recombination with free electrons (Von Hundelshausen, 1971; Bube, 1981). Due to this reason deficiency of charge carrier is created which leads to negative photoconductivity. Various compounds such as L-phenylalanine L-Phenylalaninium Perchlorate (CyracPeter et al., 2010), 2-amino-5-chlorobenzophenone (Mohamed et al., 2007), L-phenylalaninium maleate (Yogam et al., 2012), and 2-amino-5-nitropyridinium trifluoroacetate (Jovita et al., 2015) have also shown the traits of negative photoconductivity. The materials that have features of negative photoconductivity can be used as in fabrication of optical memories and switches (Aleksanyan, 1975).

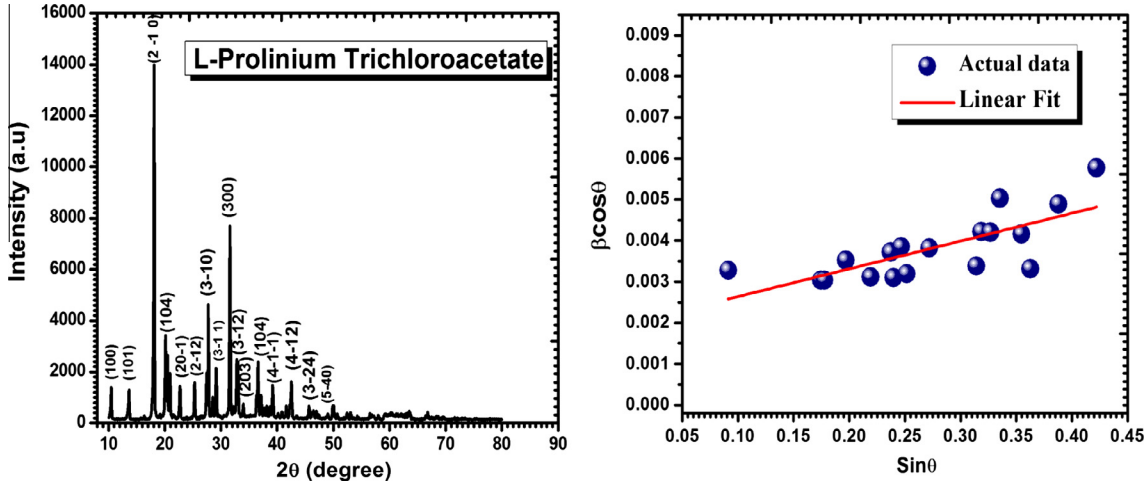

Figure 2 (a) Powder X-ray diffraction pattern; (b) strain calculation of L-Prolinium Trichloroacetate.

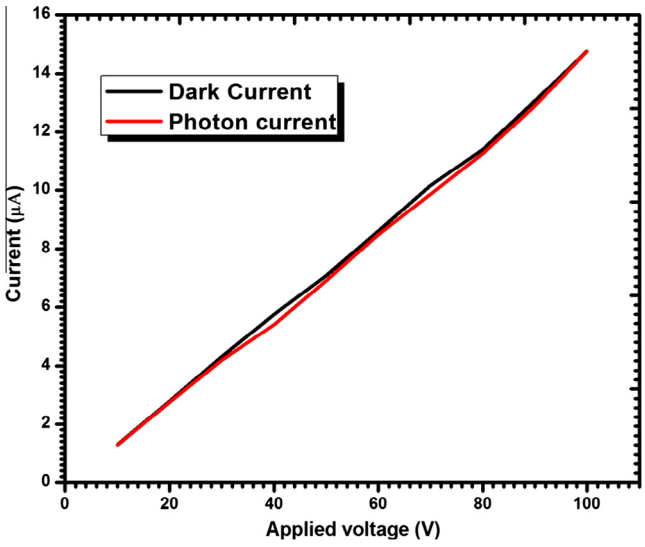

Figure 3 Variation of dark current and photon current along applied field.

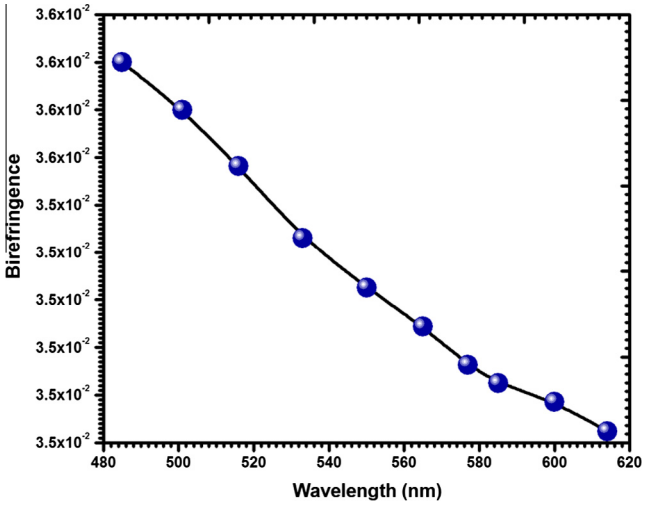

Figure 4 Graph drawn between birefringence and wavelength.

3.4. Optical homogeneity

Birefringence and related optical effects play an important role in quantum and nonlinear processes and also have been widely used in modern optical devices such as optical sensors, light modulators, liquid crystal displays, crystal filters, medical diagnostics, and wave plates (WPs) (Krishnan et al., 2014). The optically polished single crystal of LPTCA was subjected to birefringence measurements using the modified channeled spectrum (MCS) method at room temperature (Bhoopathi et al., 2013). The anisotropic effect of LPTCA crystal showed interference color fringes in the visible wavelength of range 495–615 nm. The values of birefringence have been calculated by finding the absolute fringe order for particular wavelength and computed in the relation $\Delta n = k\lambda/t$, where λ is the wavelength in nm, t is the thickness of the crystal in mm, and k is the fringe order (Peramaiyan et al., 2012). The graph drawn between birefringence Δn and wavelength (λ) is depicted in Fig. 4. The linear birefringence value of the LPTCA crystals grown at room temperature was found to be 0.03560 at the wavelength 484 nm for the thickness of 0.241 mm. The obtained experimental values show that the birefringence dispersion decreases with the increase in the wavelength of visible region, and so the grown crystal is classified as optically positive at room temperature. No notable increase in the variation of magnitude of birefringence was observed while varying wavelength from lower to higher end, and this may be explained as follows: the magnitude of optical linear birefringence values is lower in uniaxial trigonal system. Especially, the crystallographic direction of C axis having high degree of symmetry in LPTCA and also optic axis is laying on the c-axis. Due to this not only light traveling along the c-axis (Optic Axis) vibrates freely in any direction of the crystal as well as the electronic configuration is uniform for all vibration directions but also electromagnetic wave will travel faster in the ordinary axis than in the extraordinary axes. However, one obtains the reverse in negative uniaxial crystals (Pascal et al., 2011). Even though we used higher thickness for the dispersion of birefringence measurement we have got similar results. This is due to the uniaxial crystal system of LPTCA. Therefore, if the crystal is used only in harmonic generation device with a particular wavelength range, only the minimum birefringence of the crystal which causes phase matching is required. The low birefringence value ($\Delta n = 0.03541$ at $\lambda = 532$ nm) indicates that the crystal is suitable for harmonic generation device (Thukral et al., 2015b).

Table 1 Energy density at 1 pulse per sec of L-Prolinium Trichloroacetate single crystal.

Crystal	Damage threshold at 1 pulse per second	
L Prolinium Trichloroacetate (LPTCA)	7.9 J/cm^2	0.79 GW/cm^2

3.5. Laser damage threshold

During the selection of any material for optical application, laser damage threshold (LDT) has become an important criterion to be figured out. The main perspective of this technique is to find out the optical intensity or fluence up to which no damage occurs. But after this limit the crystal gets catastrophically damaged. Especially in nonlinear optical material, harmonic conversion is directly proportional to power transferred per unit area. Defects play a very major role in defining the threshold value of any compound. If the defect concentration is high, then its rigidity toward laser gets reduced. Mostly in transparent crystals optical breakdown is found, which causes laser induced damage. For the laser damage mechanism, an adequate amount of energy is absorbed to create a permanent crack over the sample. Such absorption causes the change in temperature in the irradiated region, which leads to distortion inside the structure of crystals (Thukral et al., 2015a, 2015b; Hanumantharao and Kalainathan, 2012). In case of pulsed laser, there are various factors on which laser damage threshold depends: wavelength of laser, pulse length, rate of repetition of pulse and power per unit exposed area.

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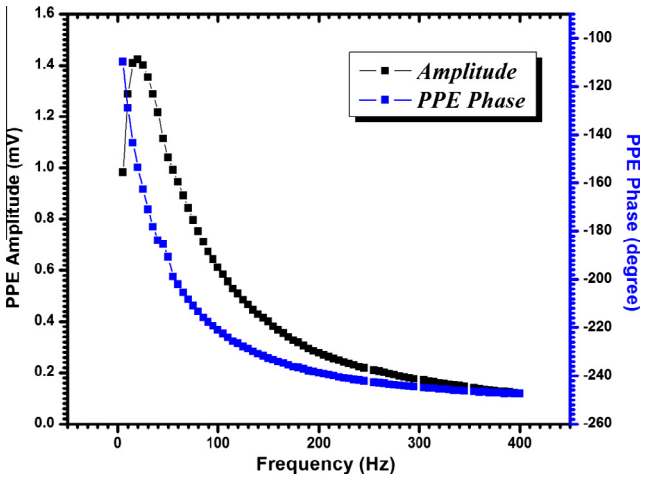

Figure 5 PPE amplitude Vs frequency curve along with phase Vs frequency curve for LPTCA single crystal.

For the title compound, Nd: YAG laser has been taken of wavelength 1024 nm with pulse rate of 10 ns as an incident beam. A fully transparent single crystal has been subjected in the path of laser with a repetition of 1 pulse per sec. The calculated value of energy density (i.e. E/A where E is applied energy and A is the focused area) is given in Table 1. The obtained value suggests that its threshold value was higher than KDP (potassium diphosphate) (i.e. 0.2 GW/cm^{-2}) (Dhas et al., 2008) and slightly lesser than urea (i.e. 1.5 GW/cm^{-2}) (Vijayan et al., 2006) which reveals that the crystal has moderate resistance toward laser. The observed value of phase matching angle for LPTCA crystal is 42 ± 1 (deg).

3.6. Thermal parameters through photo-pyroelectric technique

Apart from nonlinear optical properties, it is fundamental to know thermal parameters of the compound for application usage. Its resistance toward laser was measured by laser damage threshold technique that has been discussed briefly in above section. When the laser beam has been transmitted through the crystal, absorption takes place which results in phase transition because of heat generated inside the crystal. Due to this sake it becomes necessary to measure the thermal transport parameters of the compound which includes thermal conductivity, thermal diffusivity, thermal effusivity, and specific heat. It is simplest and non-destructive way to measure the thermo-physical characteristics of the material.

In this technique 120 mW He-Cd laser has been used with modulated chopper and acts as a source over optical transparent sample. For the pyroelectric detector, a polyvinylidene chloride (PVDC) film of thickness 28 μm has been employed. The sample was attached with the detector which was laid over thermal thick backing medium for avoiding signal fluctuations. The rear side of the sample was connected to the detector; its temperature variation was measured on rear side when the front side of the sample was irradiated by a source. To analyze the output in a more precise way a transducer was installed which converts the thermal signal into electrical. Further, the output signals are amplified and processed through lock in amplifier (Menon and Phillip, 2000). The graph has been plotted between phase of the output wave and frequency; amplitude of the output wave versus frequency is shown in Fig. 5. From the plot, the values of thermal diffusivity and effusivity have been derived and rest values were calculated. The computed values of the thermal transport parameters are tabulated in Table 2. From experimental data it was clear that its thermal stability is quite better than various compounds by comparing the specific heat values such as KDP (i.e. 857 J/kg K) (Krishna et al., 2014), Allylthiourea cadmium bromide (i.e. 776 J/kg K) (Sreekanth et al., 2013), Bismuth triborate (500 J/kg K), Zinc germanium phosphide (ZGP) (392 J/kg K) (Manivannan et al., 2008) and many more.

3.7. Mechanical stability

Nanoindentation measurement has been used as an important technique for experimental studies of the fundamental material physics. It provides a high-resolution load-displacement data, which can be used to extract many fundamental mechanical parameters of the materials. The mechanical properties of molecular solids are mostly governed by their internal structure and bond strength. In a typical nanoindentation measurement, the indenter tip is pressed into the test material's surface with a predefined loading and unloading profile and the force and displacement are recorded. Today, it is become an elementary need to assess the mechanical property before going for any device fabrication because its mechanical properties always refer physical as well as electrical properties. The basic principle of calculating hardness is defined as force applied by a nano-indenter (P) divided by contact area (H) [i.e. Hardness = P/H]. The technique not only provides the information about hardness but also elastic modulus as well as stiffness in the sample. There is a continuous measurement of depth penetration with respect to load applied. Such measurements have been taken for different sets of loads, which is the best part of the technique. It is known that organic crystals are not meant for the load bearing applications but in processing time these samples have to undergo numerous of mechanical operations. As a result, there is a practical importance behind performing this characterization (Varughese et al., 2013; Bdikin et al., 2014; Ramamurty and Jang, 2014).

The three sided pyramidal Berkovich indenter has been used to scrutinize the mechanical stability of the sample by applying various loads over it. A fully calibrated nanoindenter (TTX-NHT, CSM Instruments) was used for evaluating the mechanical parameters of the sample. The indenter impressions formed after indentation with different loads were

Table 2 Thermal parameters of LPTCA using photo-pyroelectric technique.

Sample	Thermal effusivity, e (W s^{½}/m^2 K)	Thermal diffusivity, α ($\times 10^{-6}$m^2/s)	Thermal conductivity, k (W/m K)	Sp. heat capacity, Cp (J/kg K)
LPTCA	5363 ± 31	2.99 ± 0.09	9.04 ± 0.19	2018 ± 18

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recorded using optical microscope and atomic force microscope for visualizing the surface deformations. Nanoindentation has been executed over a polished surface of plane (300) by locating indenter toward the normal direction of the sample. To estimate its mechanical strength 9 impressions have been formed over a range of force 5–150 mN. The approach speed, dwelling time and load/unload speed were kept as 2000 nm min^{-1}, 10 s and 20 mN min^{-1}, respectively. The instrument was fully controlled by the computer and complete data of load and displacement were recorded which enclosed loading segment, dwell and unloading section for all impressions. The obtained results were analyzed and interpreted using standard Oliver and Pharr method (Oliver and Pharr, 1992).

The information regarding the displacement cause in the sample while applying load over it, was given by the following relation (Doerner and Nix, 1986):

$$P = \alpha(h - h_f)^m \tag{1}$$

where P is the load applied, and a and m are the material constants, whereas $(h - h_f)$ is displacement occurring when a cycle of loading and unloading gets completed. The hardness of the single crystal was determined using the following relation:

$$H = \frac{P_{max}}{A_p} \tag{2}$$

where P_{max} is maximum load applied and A_p is projected contact area of indentation. The load independent hardness was measured by the following relation:

$$H_0 = ka_2 \tag{3}$$

where k is a constant which depends on the indenter geometry, and for Berkovich indenter, the value of k is 1/24.5 and a_2 is constant which is obtained from the polynomial fitting of peak load and contact depth plot. The slope of unloading curve can be measured as stiffness (dP/dh) which is given as follows:

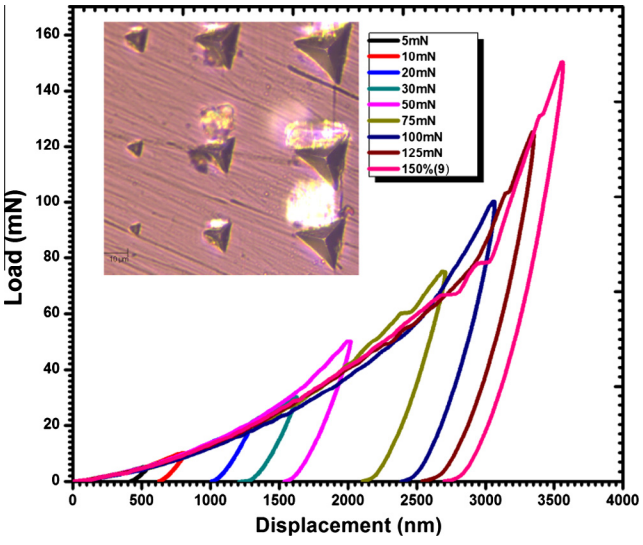

Figure 6 Load-displacement curve on the L-Prolinium Trichloroacetate single crystal along with inset of AFM images of all indentation imprints while applying nano loads.

$$h_c = h_{max} - \varepsilon \times \frac{P_{max}}{S} \tag{4}$$

Also, from Eq. (1) the value of stiffness (S) can be given as

$$s = \frac{dP}{dh} = am(h_{max} - h_f)^{m-1} \tag{5}$$

In the present case, the nano hardness has been evaluated by deploying force over a polished surface of L-Prolinium Trichloroacetate single crystal. The plot between loads applied and displacement (i.e. P-h curve) has been drawn over the range of 5–150 mN shown in Fig. 6. The characterization has been performed over the plane (300). During the time of loading, the curve will show both plastic and elastic features which interprets that deformation starts at loading state as a permanent impression on the surface. The plastic deformation occurs when the stress applied on the crystal was higher than its resistance which allows the indenter to penetrate inside the sample. The detailed mechanical behavior of the single crystal can be examined by plotting the P-h curve for individual load shown in Fig. 7. These curves suggested that the indenter forms very slight pop-in in the crystal when it was subjected for 5–50 mN load which means crystal is carrying elastic behavior up to this range. After 50 mN the pop-in concentration has been increased and it started deforming at 125–150 mN. At 150 mN the crystal starts completely deforming and reflects such an intense pop-in. In the load versus displacement plot, the displacement cause in the loading curve informs the penetration depth of the indenter. The above said behavior can be clearly visualized from the AFM images that have been shown in inset of Fig. 6. Such characteristics are common in organic compounds as they are connected with hydrogen bond and have interaction of weak Van der Waals force between the molecules. As in the title compound, it has been reported that Proline cations and Trichloroacetate anions were connected through N—H···O and O—H···O hydrogen bonds to form this molecular solid (Rajagopal et al., 2003).

Apart from mechanical responses against the loads applied, many new parameters such as young's modulus, stiffness and many more have been calculated that are tabulated in Table 3. From the recorded values, it has been observed that the contact depth is increasing w.r.t. load because the rigidity of the crystal has been decreasing with the increase in load. Such amplifications in values of contact depth were observed due to load-dependent hardness that suggests that the indentation size can affect on the hardness of material which was relative to the contact depth and peak load. The relation between the contact depth and peak load can be formulated as follows:

$$P = a_0 + a_1 h_c + a_2 h_c^2 \tag{6}$$

where P is peak load, h_c is contact depth and a_0, a_1, a_2 are the constants.

The variation between the contact depth and peak load has been plotted in Fig. 8 which was fitted using polynomial function. The value of a_2 is 2×10^{-5} mN mn^{-2}, which can be further used for load independent hardness using Eq. (3). The load independent hardness H_0 is calculated as 816.326 MPa. Fig. 9 shows the curve that has been drawn between the young's modulus and load. In the plot only four loads were taken into consideration because after 30 mN loads cracks start forming on the surface of crystal that are clearly visible in AFM images (inset in Fig. 6). It has been observed that

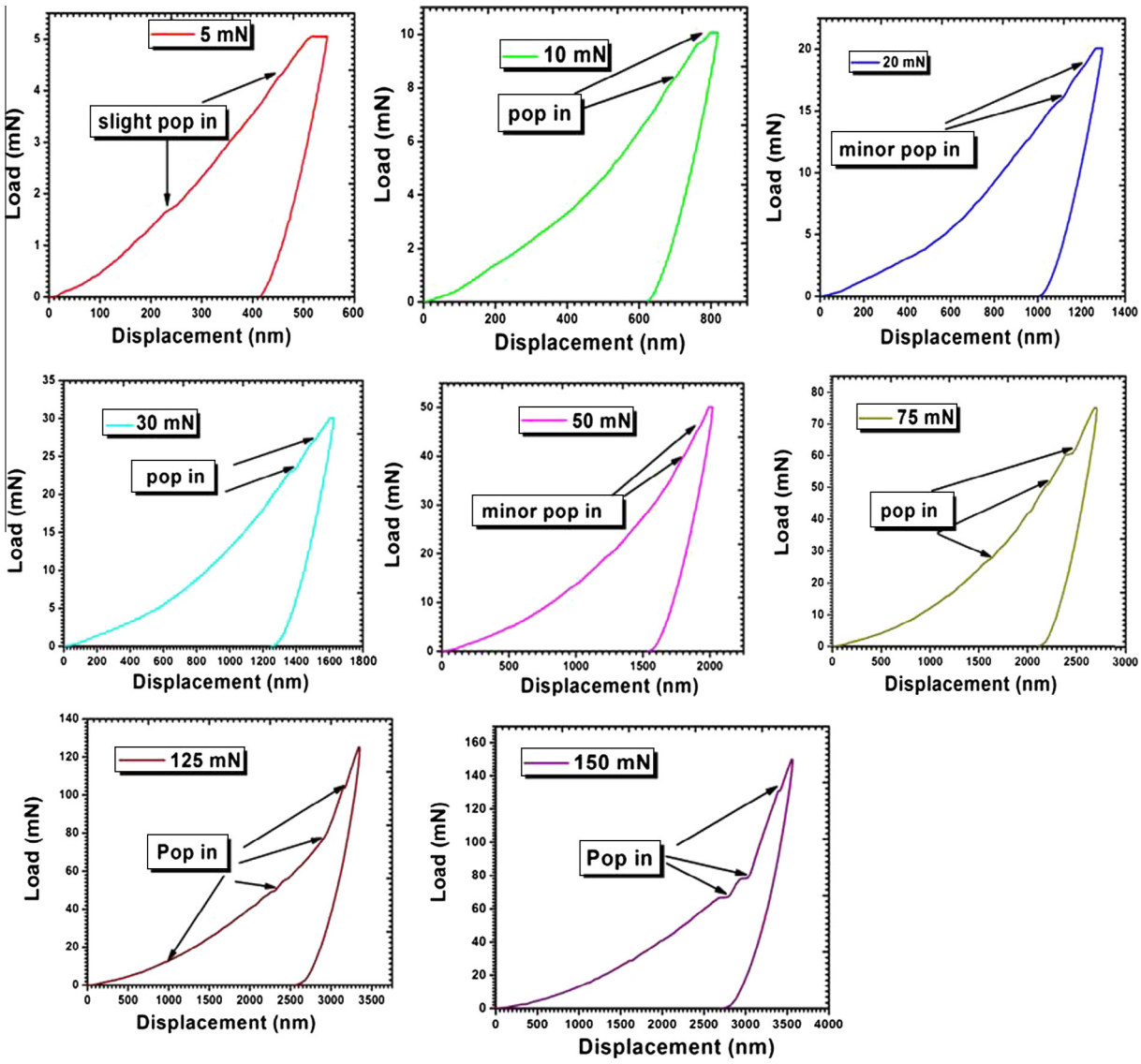

Figure 7 An individual plot of Load versus displacement of all applied nano loads.

Table 3 Various obtained parameters associated with the mechanical property of LPTCA single crystal.

(300) Plane										
F (mN)	Hit (MPa)	H_V (Vickers)	Eit (GPa)	h_m (nm)	S (mN nm^{-1})	h_c (nm)	h_r (nm)	h_p (nm)	A_P (nm^{-2})	m
5.058	899.091	83.266	19.027	546.048	0.057	478.577	457.041	417.683	5625590	1.411
10.064	793.170	73.456	16.900	819.343	0.076	718.743	686.841	629.256	12688507	1.398
20.064	613.274	56.796	14.774	1296.065	0.107	1154.129	1108.251	1020.935	32716898	1.436
30.065	578.437	53.570	14.490	1625.600	0.132	1454.694	1398.008	1283.500	51976488	1.490
50.061	633.186	58.640	14.835	2019.710	0.167	1794.129	1719.492	1575.889	79062632	1.485
75.043	514.482	47.647	13.611	2706.849	0.208	2436.902	2346.152	2163.497	145861168	1.523
100.051	525.447	48.662	15.053	3066.603	0.263	2784.285	2685.515	2460.300	190410544	1.644
125.065	548.870	50.831	15.841	3350.054	0.302	3045.805	2935.920	2643.324	227859920	1.767
150.062	582.928	53.985	16.745	3563.240	0.339	3237.398	3120.602	2811.092	257428064	1.737

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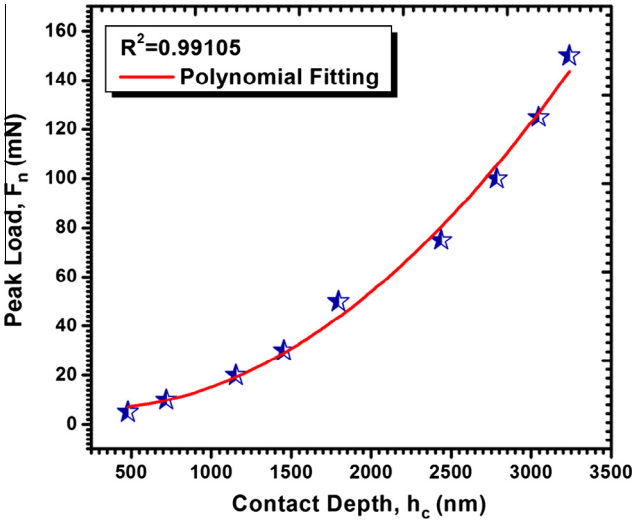

Figure 8 Variation of contact depth with peak load.

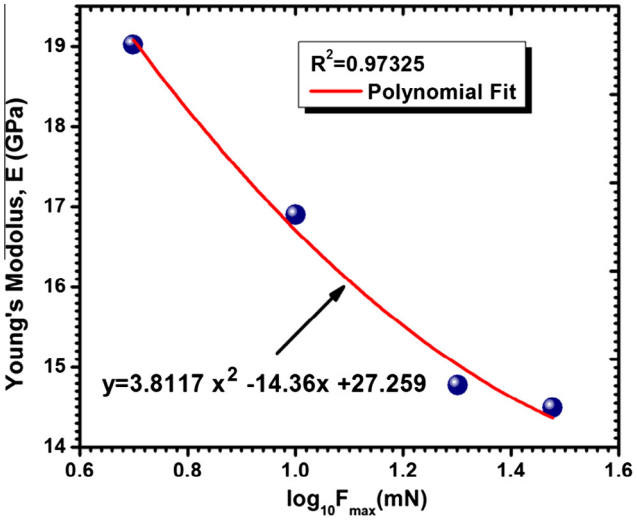

Figure 9 Variation of young′s modulus extracted from the analysis of the load-displacement curves as a function of peak load.

the young's modulus decreases with an increase in the load (Antunes et al., 2007), and this is because of the strain produced in the crystal when the load was applied by the sharp tip of the Berkovich indenter. Further, deviation in the initial loading, stiffness of the sample and contact depth are shown in Fig. 10. The relation between stiffness and contact depth is given as

$$S = a + bh_c \tag{7}$$

where a is a constant related to indentation tip rounding and the slope b is related to reduced young's modulus. Using linear fitting the value of reduced young's modulus (i.e. b) is 9.765×10^{-5} mN nm^{-2} or 97.65 GPa. With this thorough analysis, it is confirmed that the crystal carries fair mechanical properties in terms of young's modulus, hardness, and stiffness.

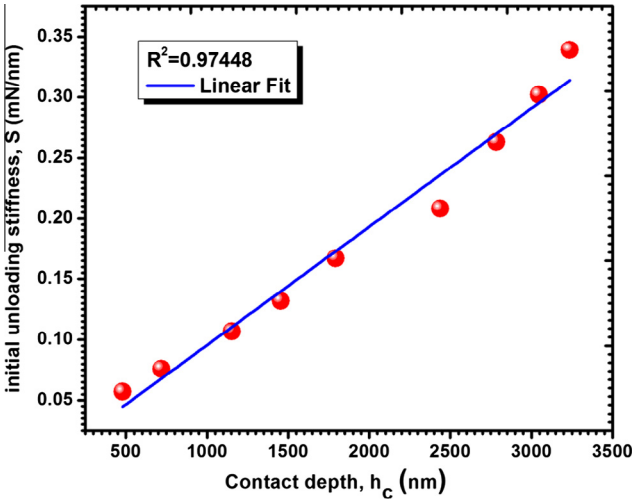

Figure 10 Variation of initial loading stiffness, S, with the contact depth at peak load.

4. Conclusion

L-Prolinium Trichloroacetate single crystal has been grown by adopting slow evaporation solution growth technique (SEST) using double distilled water as solvent in ambient condition. Single crystal XRD was ultimate tool to find out the formation of desired compound. The result reveals that the single crystal belongs to trigonal system and its lattice parameters were finely matched with reported one. The diffraction pattern has been obtained from the powder X-ray diffraction while scanning the sample over a range of 10–80°. The photoconductivity has also been observed for the LPTCA single crystal. Its optical homogeneity was examined through birefringence whereas the thermal parameters of the sample were computed through photopyroelectric technique. The rigidity toward the laser was inspected by laser damage threshold. A thorough investigation over mechanical behavior along with its different parameters was determined through nanoindentation.

Acknowledgment

The authors are highly thankful to Director, NPL for his constant support and encouragement. One of the authors (K.T) is thankful to U.G.C (University of Grant Commission) for providing the research fellowship. K.T wants to thank Dr. Sudhakar, scientist, CSIR-NPL, Delhi, for photoconductivity and Dr. B. Sridhar, scientist, CSIR-IICT, Hyderabad, for single crystal X-Ray Diffraction. Author (K.T) also wants to thank Dr. S. Natarajan, retired scientist, Department of Physics, Madurai Kamaraj University, Madurai, for continuous support and guidance. Budhendra Singh would like to express his personal thanks to FCT (Fundaçãopara a Ciência e a Tecnologia) for post-doctoral research grants with reference numbers SFRH/BPD/76184/2011.

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Please cite this article in press as: Thukral, K. et al., In-depth behavioral study of l-Prolinium Trichloroacetate single crystal: An efficient candidate for NLO applications. Arabian Journal of Chemistry (2016), http://dx.doi.org/10.1016/j.arabjc.2016.09.011