

# Characterization and Evaluation of properties of Nicotinium p-Toluenesulfonate Monohydrate (NPT) Crystal

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## ABSTRACT

Researchers have shown considerable enthusiasm for investigating novel organic materials that have the potential to show pharmaceutical and NLO effects. Due to its vital function in effectively treating human illnesses, nicotinic acid, a key hydrophilic molecule included under the vitamin B complex, has garnered considerable attention in the pharmaceutical sector. During the current investigation, a good quality nicotinium p-toluenesulfonate monohydrate (NPT) single crystal was obtained with the help of SEST by taking equimolar amounts of nicotinic acid (NA) along with p-toluenesulfonic acid. Structural characterization of NPT was performed by PXRD and the structure found well in accordance with the literature. The performance of NPT was assessed using various techniques. These investigations confirm its potential as a highly promising material with significant implications for a diverse range of applications in the field of NLO applications.

**Keywords-** Crystal Growth, Dielectric, Nanoindentation

## I. INTRODUCTION

Numerous investigations in the area of NLO materials have been conducted since Townes et al. invented the laser in 1955. Within this field, when intense light is passed through an optical medium, new photon with varying photon energies are produced and along with this, coherence of the input light is also preserved. Two main nonlinear optical processes include SHG and THG which involve the generation of photons with doubled and tripled optical frequencies of the original light respectively [1,2]. Many of the crystal's properties are greatly influenced by its structure and symmetry.

Constant efforts are being made by researchers to find reliable and high-quality materials. They have successfully designed and synthesized various types of organic materials based on single crystal like materials containing D- $\pi$ -A interactions. In fact, the presence of a polar  $\pi$ -conjugated bond facilitates the formation of a push-pull conjugated structure with donor at one end and acceptor at the other which facilitates the asymmetric charge distribution [3,4]. The kind of substituent (donor or acceptor), solvent polarity and temperature play a significant role in these conjugated intramolecular charge transfer (ICT) compounds [5-8].

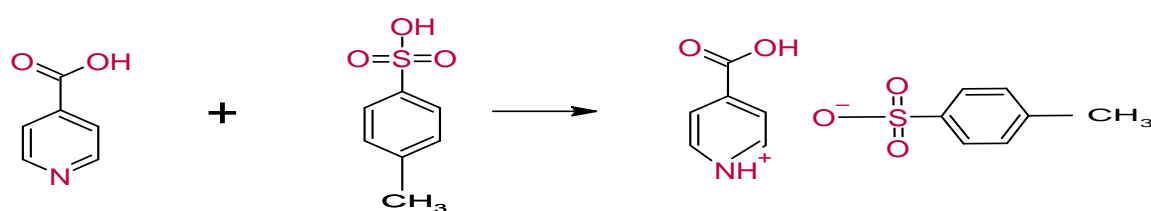
Few researchers emphasize their research on the drug molecule Nicotinic acid (Niacin). It is a widely recognized hydrophilic pharmaceutical compound within the vitamin B complex group which is famous for its substantial therapeutic significance in addressing human diseases such as pellagra and shows many different pharmaceutical effects [9,10].

p-toluenesulfonic acid (tosylic acid) stands out as a formidable organic acid due to its remarkable NLO properties which arise from the considerable electron cloud delocalization within the sulfonate group of p-toluenesulfonate. Hence, its various derivatives are synthesized and analyzed for applications in multidisciplinary areas. Several previously reported crystals of p-toluenesulfonic acid show good NLO activities.

In this manuscript, we detail the preparation and growth of a hydrogen-bonded charge transfer (CT) complex of nicotinic acid (organic base) and p-toluenesulfonic acid (organic acid) thereby resulting in the formation of a non-centrosymmetric crystal lattice with commendable NLO characteristics. In the course of the proton transfer process, a proton takes place from the electron donating moiety of p-toluenesulfonic acid to the electron accepting group of nicotinic acid to form a zwitterion and also shows improved thermal and mechanical stability through hydrogen bonding interactions. Hence, it is projected as a forefront candidate for NLO applications. This article assesses various aspects of NPT single crystals in order to judge its applicability in device fabrication.

## II. EXPERIMENTAL

The starting materials p-toluenesulfonic acid monohydrate and Nicotinic acid obtained from CDH Company, are dissolved in distilled water in an equimolar ratio (1:1). The solution was subjected to continuous magnetic stirring for a duration of 4 hours resulting in the formation of a homogeneous solution. This was subsequently filtered to eliminate impurities and allowed to undergo evaporative drying at ambient temperature. After a few days nucleation started and subsequently, got the transparent single crystals in five weeks. Fig. 1 presents the photograph of the obtained crystal. The scheme for synthesis of nicotinium p-toluenesulfonate monohydrate (NPT) is as follows:



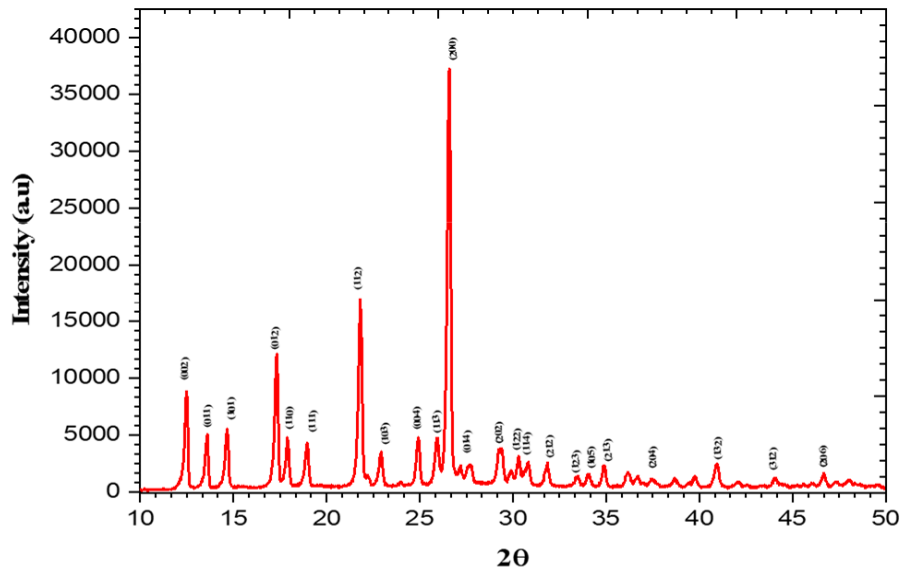
**Fig. 1** Picture showing NPT single crystal

## III. Results and discussion

### A. PXRD

PXRD has recently emerged as the most effective characterization method for structural investigation. The fundamental principle of X-ray diffraction theory lies in the phenomenon of constructive interference exhibited by monochromatic X-rays. The formed crystals were powdered and subjected to XRD having  $\lambda$  as 1.541836 Å to study the structure of the titled compound. The  $2\theta$  is varied from  $10^\circ$  to  $50^\circ$  with a step size of  $0.02^\circ$ . The depicted Fig. 2. illustrates the recorded pattern obtained through PXRD.

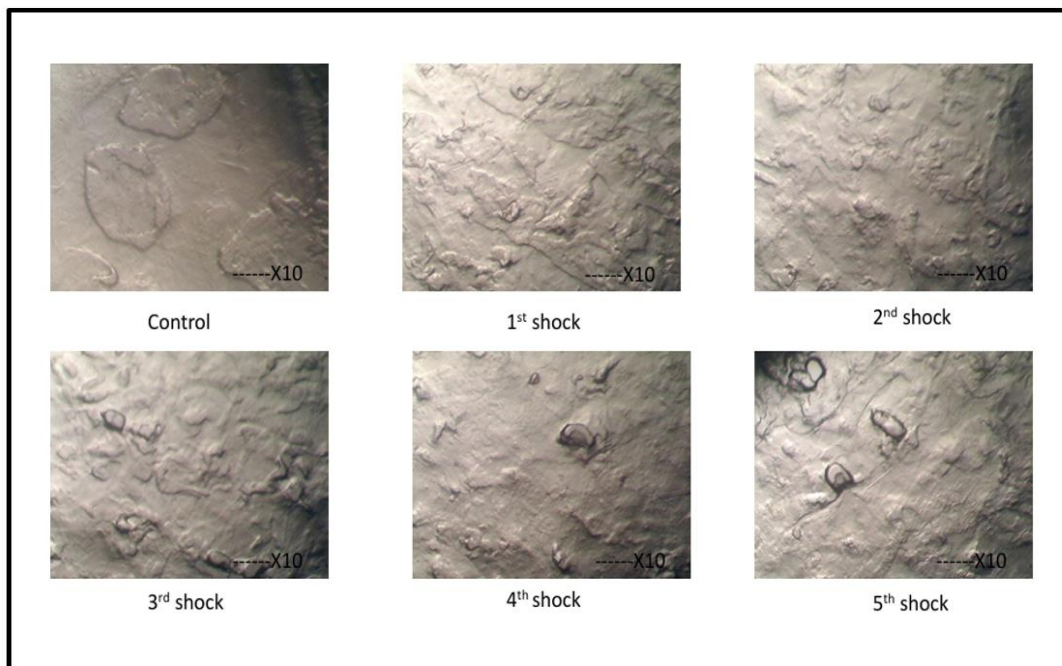
The experimental peaks were observed and exhibited excellent concurrence with the literature findings [11].



**Fig. 2** PXRD plot for NPT crystal

### B. Shock damage threshold

In this contemporary era, the study of materials subjected to shock wave is becoming a popular area of study in the field of material science. It is a high-pressure phenomenon that is observed in events like volcanic eruptions, swiftly moving airplanes etc. It is one of the straight forward methods for studying the behaviour of materials under harsh conditions and for modifying their behaviour without changing the original crystal system. Shock waves can cause structural defects, phase shifts, orientation changes etc. in crystalline materials [12-13]. This study involves an investigation of the sample when exposed to shock waves up to Mach numbers 1.7 on NPT crystals using a shock tube. On increasing the shock, eventually cracks start to appear. The sample was subjected to XRD to observe the effect of shock waves on the crystalline sample.



**Fig. 3** Optical microscope images of the surface of the crystal with 4X magnification (a) Cleaned surface with solvent; (b) surface followed by 1st shock; (c) surface followed by 2nd shock; (d) surface followed by 3rd shock; (e) surface followed by 4th shock; (f) surface followed by 5th shock for NPT crystal

## Surface morphology studies

Studies of surface morphology offer a fast and easy technique to identify surface defects, flatness or etch patterns. As a result, it makes a significant contribution to the materials' characterization under harsh conditions and an optical microscope is utilized to view the surface. Fig. 3 shows the optical micrographs (4×) for control and when subjected to shock waves of NPT crystals. The test crystal bent and showed defects that kept on increasing with progressive shocks and after 5<sup>th</sup> shock, it cracked.

## Structural properties

It is possible to observe the changes occurring in structure-related characteristics of the crystals by examining the effect intense radiations or changing physical environments on them. In the present study, the sample was subjected to XRD having  $\lambda = 1.5407 \text{ \AA}$  for  $\text{CuK}\alpha$ . The observed pattern for the sample before and after exposure to shock waves is shown in Fig. 4.

The obtained profiles provide conclusive evidence that NPT crystal does not undergo a structural phase change and no new crystalline peak creation nor a peak disappearance has been seen. But a high degree of structural disorder is seen and peaks observed on successive shock wave conditions show an increase in full width half maximum (FWHM) on increasing shocks [14,16] which is shown in Fig. 5. All these may be caused due to increased misalignment in the atomic lattice plane, atomic displacements and modifications in the bonding scheme brought on by the influence of shock waves.

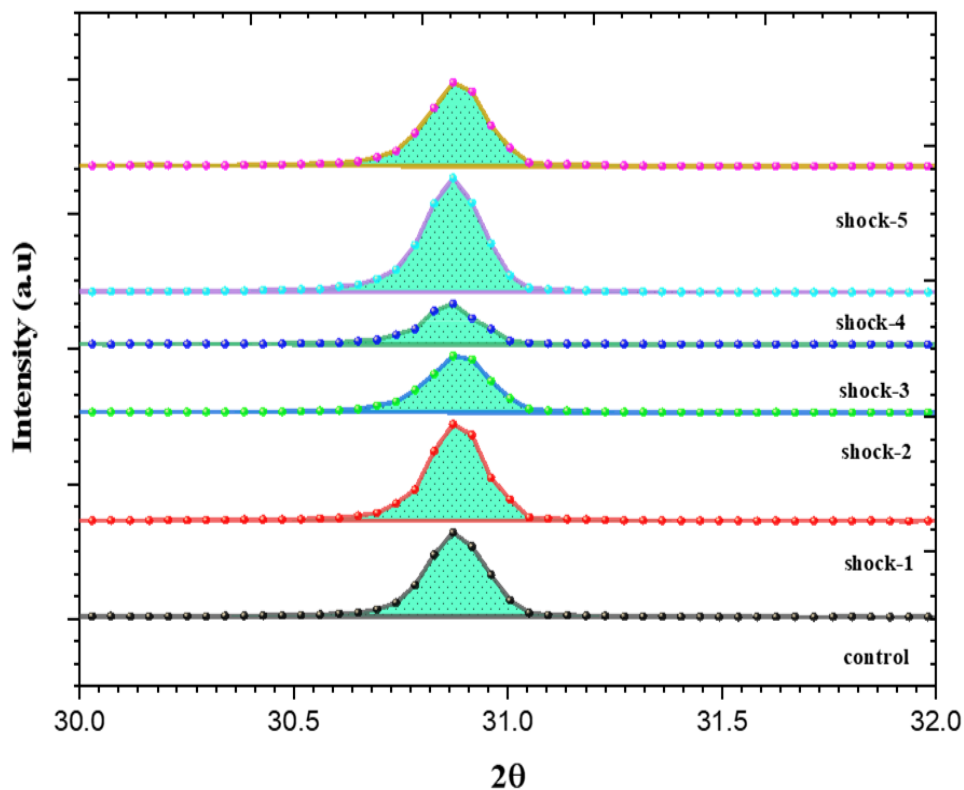
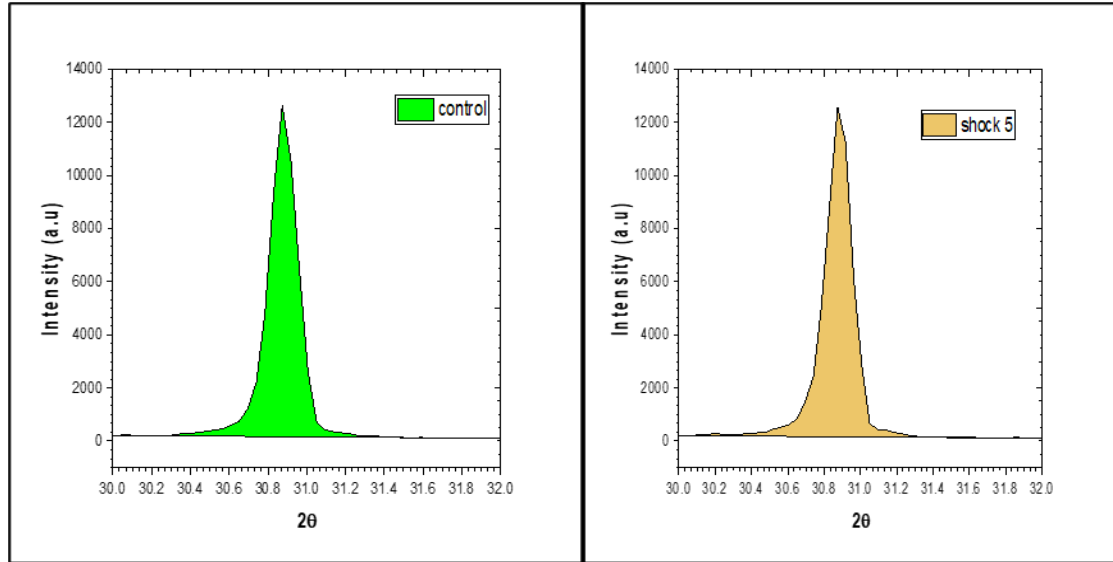


Fig. 4 XRD plot before and after exposure to shock wave for NPT crystal



**Fig. 5 Comparison of XRD pattern of control and post 5th shock wave for NPT crystal**

### C. Nanoindentation

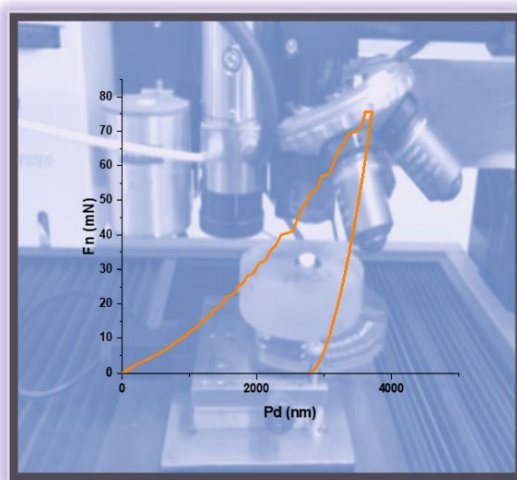
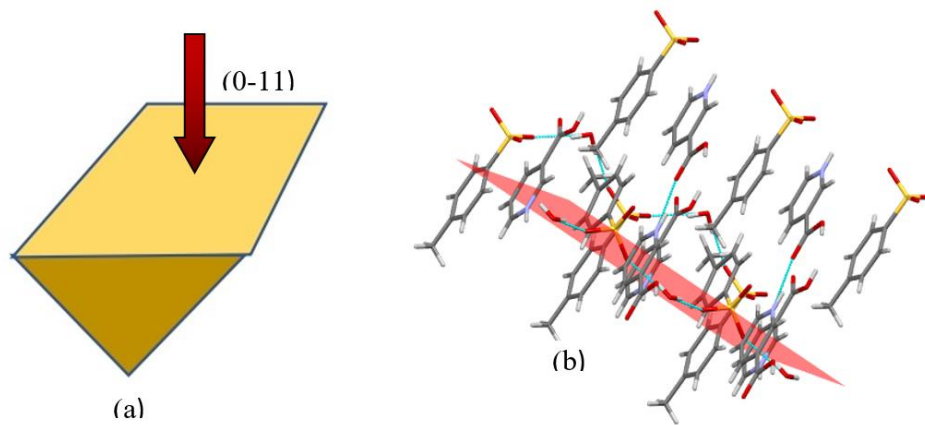
In recent times, engineers have shown increased interest in the nanoindentation technique, which involves evaluating the hardness-related parameters of single crystals. This technique allows for the correlation of measured properties with the underlying structural properties and intermolecular interactions. The findings obtained from these evaluations have numerous technical applications, including metallurgical industries, pharmaceuticals and molecular electronics [17]. The direction of the slip planes, twinning planes and cleavage planes on application indentation load determine the mechanical behaviour of single crystals. The nanoindentation technique uses the P–h responses for loading and unloading sequences for different loads in mN for measuring mechanical properties. This method can be used to investigate aspects such as anisotropy in molecular contacts, shear stability, evaluation of structural inhomogeneities and stiffness of various bond types. In terms of studying a material’s behaviour mechanically, its stiffness, strength and toughness are the fundamental properties. These characteristics provides indication of the material's resistance to cracking, as well as its ability to withstand elastic and plastic deformations. The most popular method for doing this is proposed by Oliver and Pharr which uses Berkovich tip nanoindenter. The schematic for the process of nanoindentation is presented in Fig. 6.

In the current study, a well-polished single NPT crystal (plane (0-1 1)) was placed below a Berkovich tip and exposed to varying loads between 5 to 150 mN at an approach rate of 2000 nm/min approach rate. The indenter was well-calibrated from TTX-NHT, CSM Instruments. The P-h curves for different loads are presented in Fig. 7 Any surface changes caused by the indenter to the crystal, such as dents and fissures, can be seen using the AFM technique.

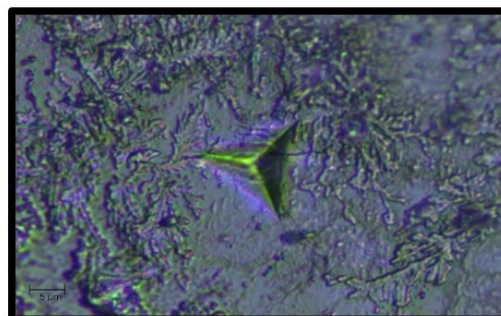
The plastic ( $h_p$ ) and elastic ( $h_e$ ) deformations cause the total contact depth ( $h_t$ ). These are then related to the hardness of the sample. In materials where no phase transition takes place, the plasticity of the sample is attributed to the accumulation of material and the dislocation activity. As can be seen, the load-depth profiles are continuous and smooth during the curves with no noticeable pop-ins or pop-outs for maximum loads less than 20 mN. This shows that sample experiences elastic-plastic deformation at loads upto 20 mN without noticeable microcracking. But on increasing load over 20 mN, the noticeable pop-in are observed which keep on increasing upto 150 mN. This shows that the broad elastic-plastic deformation for a single crystal becomes substantial up to indentation stresses of 30 mN without cracking. The mechanical parameters for NPT crystal are tabulated in table 1.

From the load-displacement curve it is evident that the crystal develops a micro-crack above 20 mN. Furthermore, the variation of modulus with load is exhibited in Fig. 8, which can be related to the ISE of the indenter and the intrinsic deformation. Also,  $h_c$  variation with  $f_{max}$  curve is shown in Fig. 9. Furthermore, load independent hardness ( $H_0$ ) can be determined using the expression

$$H_0 = Ka_2, \text{ using } K = 1/24.5 \text{ for berkovich indenter} \quad (2)$$



(c)



(d)

**Fig. 6** The schematic for the process of nanoindentation for NPT crystal (a) crystal morphology; (b) (0-11) plane; (c) load displacement graph; (d) indentation mark on the surface of NPT crystal



And  $a_2$  obtained from the slope of the polynomial fitted graph for the given relation

$$F_{max} = a_0 + a_1 h_c + a_2 h_c^2 \quad (3)$$

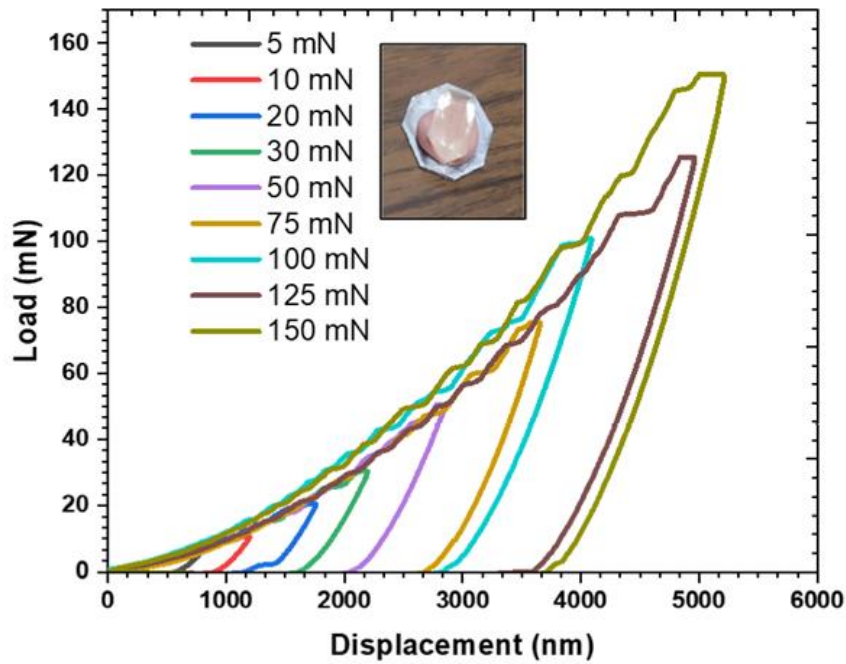


Fig. 7 The P-h curves for different loads for NPT crystal. The inset shows NPT crystal used for nanoindentation

**Table. 1 Mechanical parameters calculated from loading and unloading curve of NPT single crystal**

Fm (mN) (nm <sup>2</sup> )	Hv	HIT (MPa)	EIT (GPa)	S (mN/nm)	h <sub>c</sub> (nm)	m	h <sub>m</sub> (nm)	h <sub>r</sub> (nm)	h <sub>p</sub> (nm)	Poisson's ratio(σ)	Ap
5.54	79.108	854.19	12.363	0.0379	658.2951	1.36	771.17	624.314	595.723	0.30	6320415.2
10.59	77.979	842.01	11.688	0.0558	1071.713	1.39	1215.97	1022.47	845.062	0.30	1.34718E7
20.46	76.847	829.78	11.064	0.0711	1506.058	1.42	1708.53	1436.00	1176.65	0.30	2.45076E7
30.35	75.712	817.52	10.490	0.0828	1942.581	1.44	2233.60	1845.42	1571.90	0.30	3.78278E7
50.50	74.573	805.22	9.9674	0.0976	2506.347	1.46	2891.22	2381.06	2154.36	0.30	6.27329E7
75.48	73.430	792.88	9.4953	0.1161	3056.018	1.48	3542.69	2894.57	2558.61	0.30	8.93781E7
100.79	72.283	780.50	9.0739	0.1288	3661.352	1.49	4249.30	3465.57	3058.75	0.30	1.30079E8
125.44	71.133	768.08	8.7034	0.1420	4132.801	1.50	4799.79	3910.31	3460.77	0.30	1.65927E8
150.69	69.979	755.62	8.3837	0.1540	4520.837	1.50	5252.17	4277.20	3810.46	0.30	2.01888E8

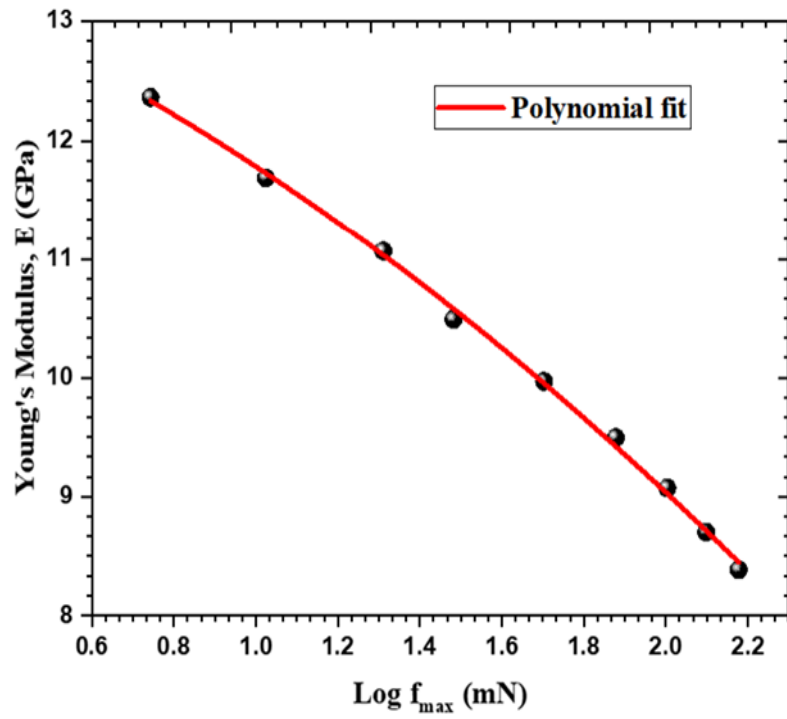


Fig. 8 Variation of Young's Modulus with Log of peak load for NPT crystal

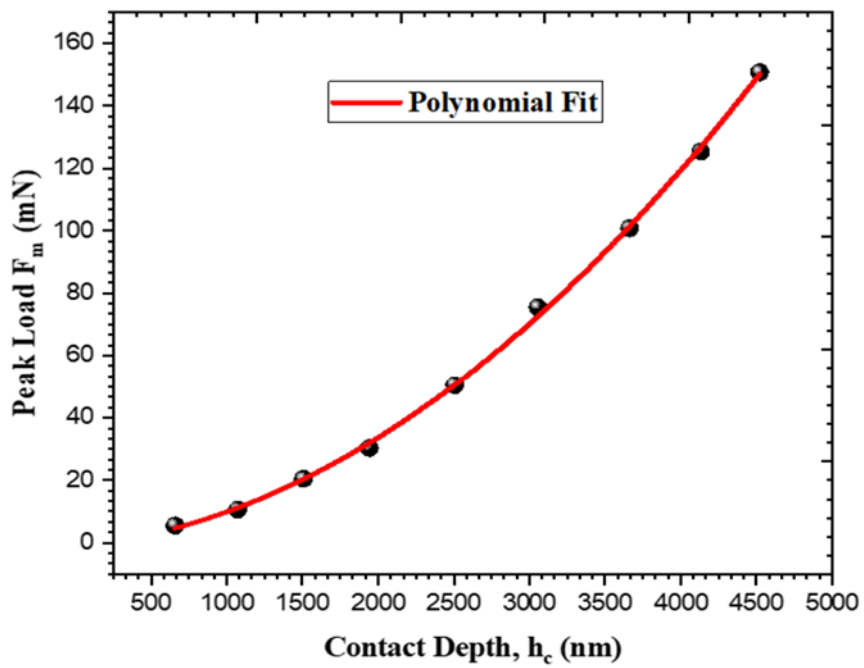


Fig. 9 Variation of  $h_c$  with peak load for NPT single crystal

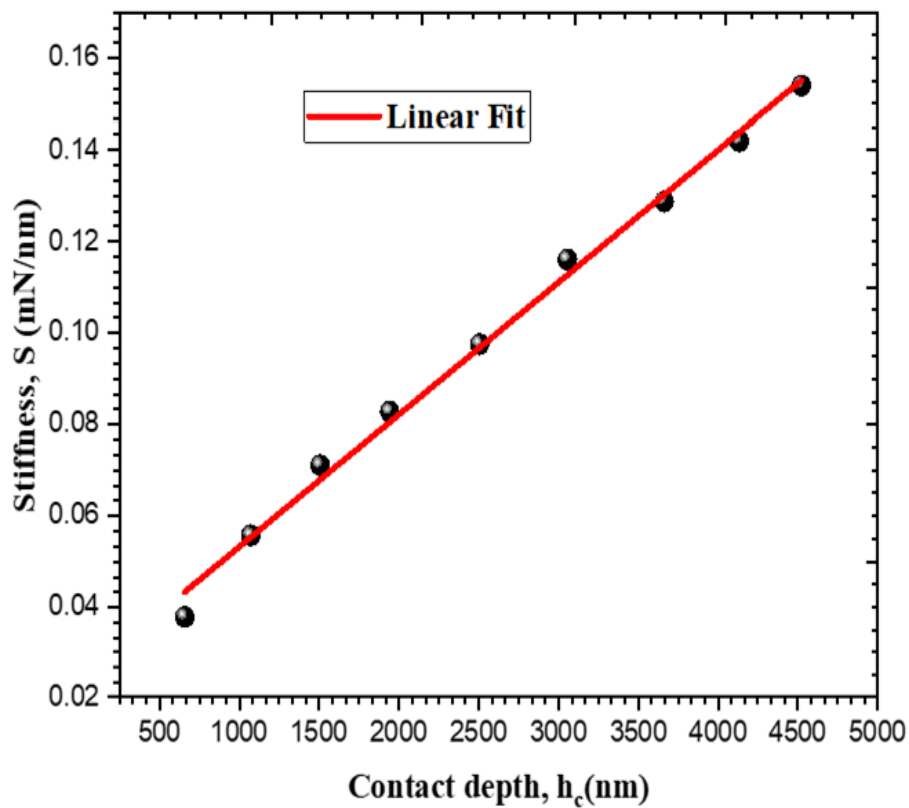


Also, Fig. 10 shows a linear relationship of stiffness  $S$  with  $h_c$  for NPT single crystal which are related as

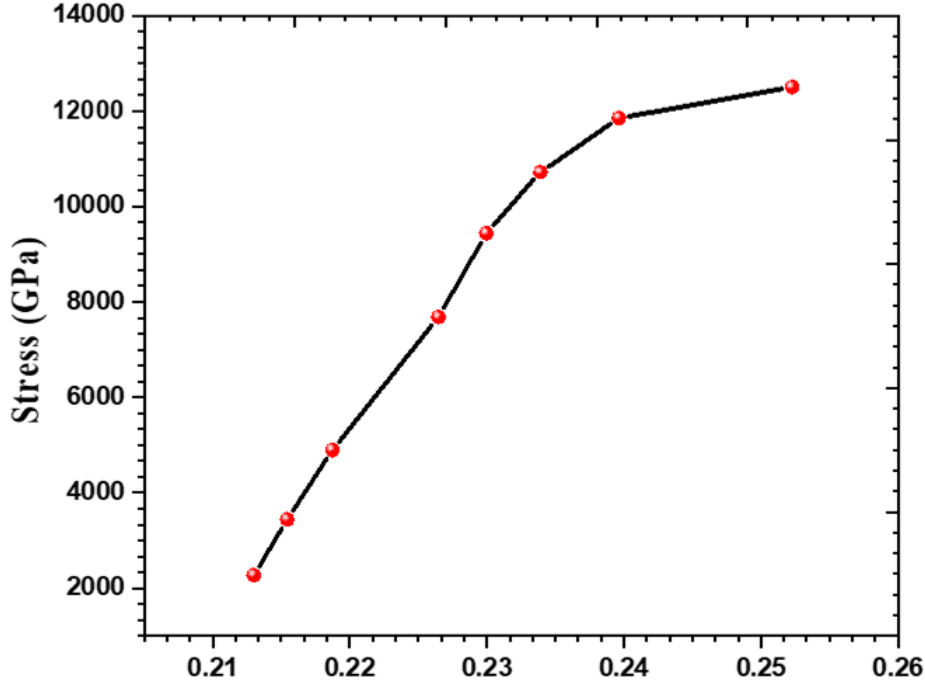
$$S = a + bh_c \quad (4)$$

herein 'a' represents a constant for the particular the indentation type while 'b' denotes the slope of the indentation created on the NPT single crystal. Experimental findings revealed an intercept (a) of 0.024. Employing a linear regression analysis to elucidate young's modulus. The slope was found to be  $2.892 \times 10^{-5} \text{ mN nm}^{-2}$ . So, the reduced young's modulus was estimated to be 28.92 GPa.

In addition to this, a stress-strain is plotted using the above data which is shown in Fig. 11. On fitting the polynomial curve, the coefficient  $a_0$ ,  $a_1$  and  $a_2$  were obtained. So,  $a_2$  obtained is  $6.347 \times 10^{-6} \text{ mN nm}^{-2}$ . Also, eqn. 2, gives the independent hardness as 0.258 GPa or 258 MPa. So, the titled compound offers a high resistance to deformation [18-20].



**Fig. 10** Variation of Stiffness with peak load for NPT single crystal



**Fig. 11 stress-strain relation for NPT single crystal**

#### **D. Impedance studies**

The dielectric analysis also provides the details on the location of grain boundaries, the amount of impurities and the presence of crystallographic defects [21-25]. In the present context, the dielectric parameters were studied for NPT crystal having thickness of 1mm by varying temperature from 30-60°C for 20 Hz–200 MHz frequency. At first, silver paste was put on both side of the crystal to make good electrical contacts and the potential difference of 1 V was kept during the experiment for the parallel plate capacitor. The dielectric constant ( $\epsilon'_r$ ) can be obtained as

$$\epsilon'_r = C_p d / \epsilon_0 A \quad (5)$$

$C_p$ ,  $A$ ,  $d$ ,  $\epsilon_0$  ( $8.85 \times 10^{-12}$  F/m) are the capacitance, area, thickness and permittivity of the material respectively. It analyses the ability of materials to store electrical energy.

#### **Dependence of dielectric constant on temperature**

$\epsilon'_r$  almost remains constant with the temperature at elevated frequencies. However, at low frequencies,  $\epsilon'_r$  at 40°C slightly rises, as illustrated in Fig. 12, then returns to constant with rising temperature. This can be a result of structural modifications due to a change in contact strengths at intermediate temperatures. Water, being a polarized molecule, significantly impacts the crystal's dielectric properties. The molecular dipole orientation remains unchanged at lower temperatures due to intact bonds.

As the temperature increases to 40°C, the strength between contacts weakens, allowing water molecules to realign themselves. This realignment is reflected with a rise in  $\epsilon'_r$ , particularly at smaller frequencies where polarization effects are more pronounced.  $\epsilon'_r$  eventually attains a stable value of 27 as the temperature continues to rise, indicating reduced polarization effects due to molecule dehydration.

### Frequency dependent variation of dielectric constant

Its normal dielectric behaviour is illustrated in Fig. 13 in which the value of  $\epsilon_r'$  decreases on increasing frequency which is influenced by the polarisation mechanisms. At low frequencies, the space charge polarization is the main polarisation mechanism which contribute to the value of  $\epsilon_r'$ . Furthermore, the molecular dipole moments exhibit an enhanced responsiveness to the externally induced electric field [26]. With the increase in frequency, the contributions from different polarizations in the material start to decrease. The molecular dipole moments within the material are unable to respond quickly enough to the rapid changes in the applied electric field. Consequently, this results in a drop in capacitance and consequently, a drop in  $\epsilon_r'$  value of the material. This constant value is attained at a higher frequency may be correlated to the material's structure and its polarization. The lower value of  $\epsilon_r'$  signifies the good quality of the NPT crystal.

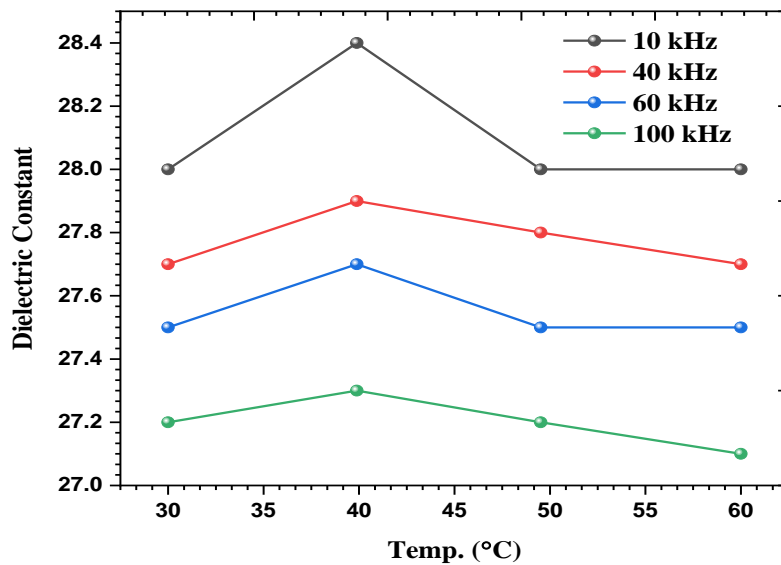


Fig. 12 dielectric constant variation with temperature for NPT single crystal

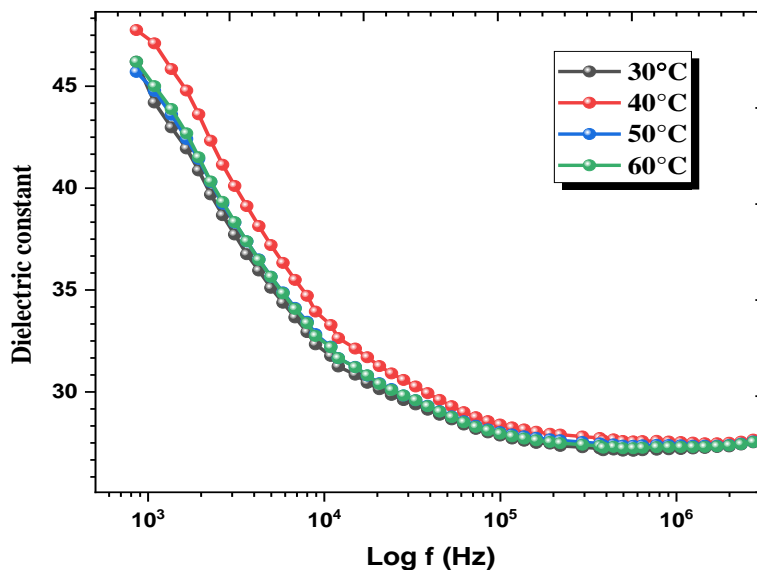


Fig. 13 Plot for frequency dependent variation of dielectric constant for NPT single crystal

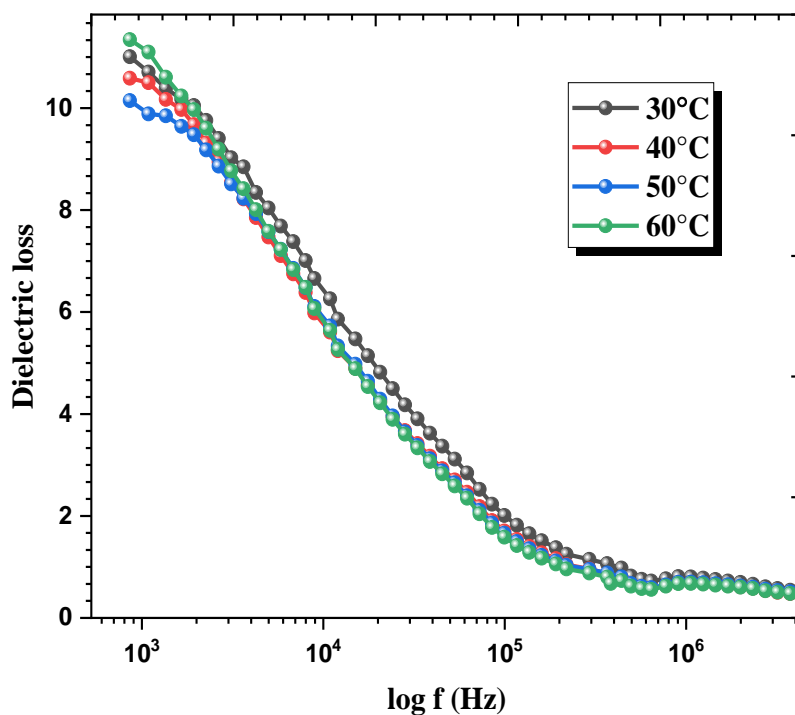
Furthermore, the slight variations observed in  $\epsilon_r'$  value with the temperature is attributed to the contribution of molecular permanent dipole moment in the process of polarization [27]. Its low dielectric constant value makes it a good photonic and electro-optic device material.

### Frequency dependent variation of dielectric loss

The imaginary part of  $\epsilon_r'$  measures dielectric losses which can be calculated using the formula

$$\epsilon'' = \epsilon_r' \times \tan \delta \quad (6)$$

The relationship between dissipation ( $\tan \delta$ ) and the frequency of the applied field is illustrated in Fig. 14 which shows a normal trend of decrease in dissipation with increased frequency. The good quality of the titled material is indicated by the low value of the dielectric loss. This loss factor, which is inversely proportional to its conductivity, represents the energy used to align the dipoles. As the frequency increases, the dipoles within the material gradually lose their ability to respond effectively to the rapidly changing electric fields. This leads to a decrease in their receptivity to such fields, resulting in a change in the value of dissipation with frequency [28].



**Fig. 14 impact of frequency on dielectric loss behavior for NPT single crystal**

### A.C conductivity ( $\sigma_{ac}$ ) and impedance

The electrical conductivity is given as:

$$\sigma(\omega, T) = \sigma_{dc}(T) + \sigma_{ac}(\omega, T) \quad (7)$$

where the  $\sigma_{dc}$  elucidates the temperature-dependent dc conductivity and  $\sigma_{ac}$  which is ac conductivity. Electrical conductivity is a defect-controlled process and studying this can provide important insights into the mobility, development and movement of lattice defects in hydrogen-bonded crystals [29]. The ac conductivity ( $\sigma_{ac}$ ) of NPT crystals exhibits a pronounced frequency dependence of the applied ac field for varying temperatures shown in Fig. 15.

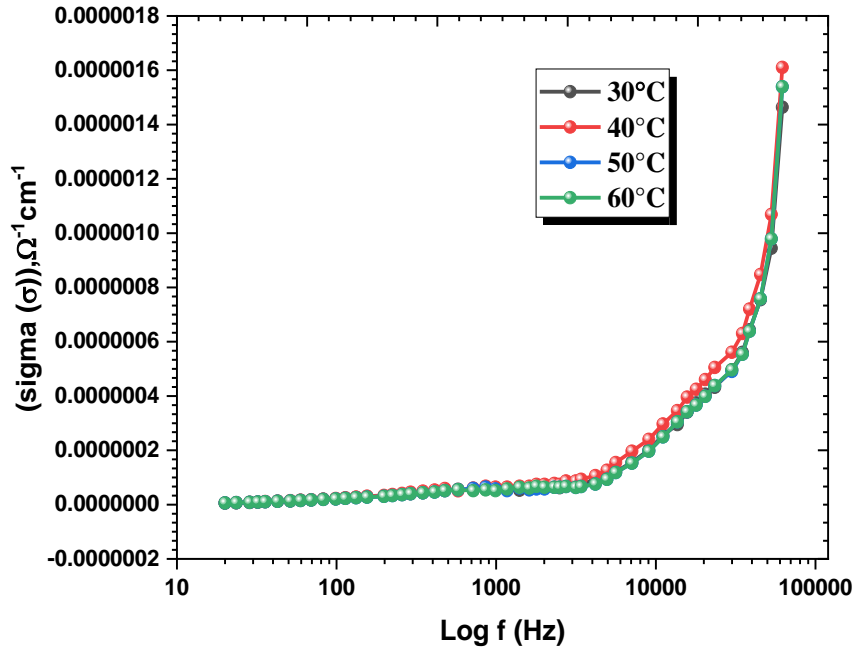


Fig. 15 Variation of Sigma with Frequency for NPT single crystal

The ac conductivity is negligible at low frequency upto 100 kHz and then increases and attains maximum value. This can also be obtained from dielectric loss as

$$\sigma_{ac} = \omega \epsilon_0 \epsilon_r' \tan \delta \quad (8)$$

here  $\tan \delta$  represents the dielectric loss.

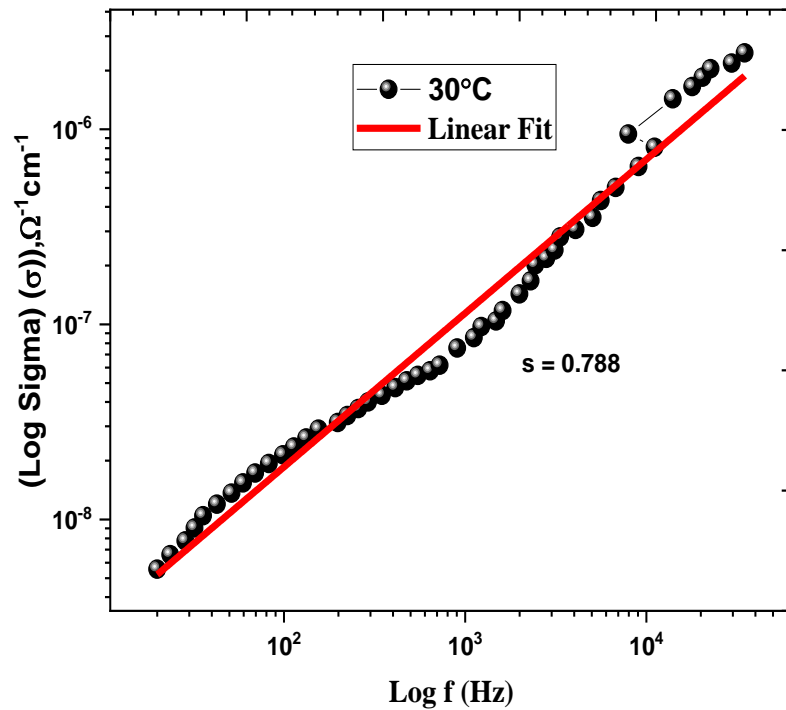


Fig. 16 Frequency dependent variation of Log(Sigma) for NPT single crystal

The experimental results are justified by using different theories. One such theory is the polaron hopping model. According to this, the proton–phonon interaction occurs on the path of the proton and exhibits a strain field forming a quasi-particle like a polaron. The  $\sigma$  leads to greater values at longer frequencies at a given temperature. This trend supports the polaron hopping mechanism in NPT crystals. At higher frequencies, the polaron disperses and the protons travel forward, adding to the conductivity. Jonscher’s universal power law relates  $\sigma_{ac}$  with  $\omega$  as

$$\sigma(\omega) = A\omega^s \quad (9)$$

where A is a constant,  $\omega$  denotes the angular frequency and "s" is a dimensionless quantity which is almost independent of temperature and measures how much the mobile ions interact with the lattice [30-32]. The slope of the graph exhibited in Fig. 16 gives  $s = 0.788$ .

### Impedance analysis

It is a versatile approach to assess different electrical parameters of various ion conducting solids. It gives vital information about the bulk and surface properties of these materials. Fig. 17 demonstrates the frequency-dependent variation of impedance ( $Z'$ ) across varying temperatures for NPT crystal.

The graph shows that  $Z'$  has inverse relation with frequency and temperature. For larger values of frequencies, it shows a constant value which can potentially be attributed to the release of space charge.

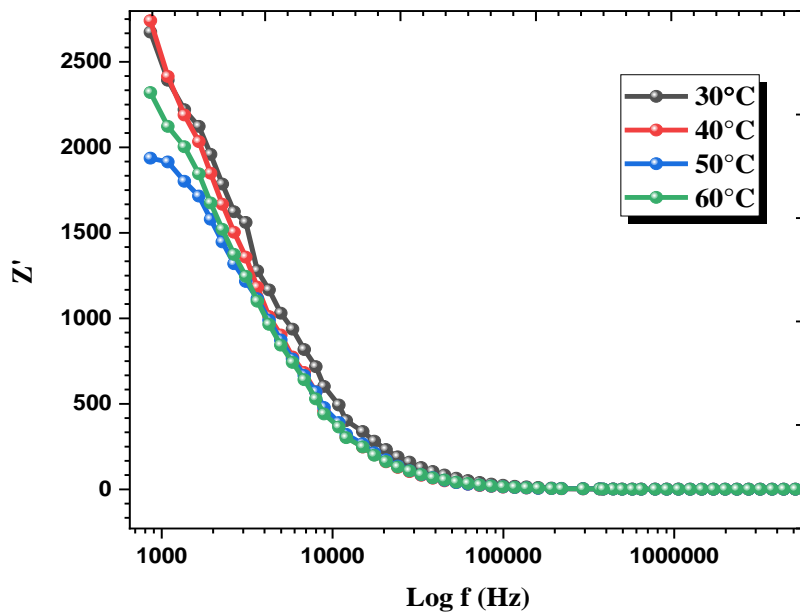


Fig. 17 Variation of impedance with Frequency for NPT single crystal

## IV. CONCLUSIONS

The transparent organic NPT single crystals were grown and subjected to various characterizations in order to access its potential applications. PXRD analysis of the crystal unfolds the information about its space group and lattice parameters which were found to be same as in literature. Nanoindentation results manifested the better endurance and mechanical strength of the title compound. The SDT for NPT on impulsion of shock waves was determined. Its various dielectric parameters were also investigated. These findings prove it to be a promising material for NLO applications.

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