Discussion on Structural, Optical, Thermal, Mechanical, Dielectric and Third-Order NLO Properties of 3-Nitroanilinium Chloride Single Crystals for Optoelectronic Applications

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Research Article

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Abstract

Preferable, third-order nonlinear optical (NLO) single crystal, 3-Nitroanilinium chloride (3NACL) was auspiciously synthesised by slow evaporation technique. The crystal system of synthesised 3NACL crystal is triclinic with centrosymmetric space group

was identified by single crystal XRD studies. All the functional groups present in the sample and its respective vibrations are analysed through FTIR analysis. UV-Vis transmittance spectrum revealed that the synthesised material was 83% transmittance and it cut-off wavelength was 276nm. The mechanical stability and thermal property of grown 3NACL crystals were ascertained by Vickers micro hardness analysis and TG/DTA analysis. The intermolecular interaction of the 3NACL was scrutinized by Hirshfeld surface analysis. Dielectric studies revealed that dielectric constant and dielectric loss were high at lower frequency region due to the space charge polarization. Inclusion free 3NACL crystal was used to analyse the Laser damage threshold (LDT) studies and its calculated LDT value was 4.3 GW/cm^2. The third-order NLO parameters (β = 7.5472x10^{-12} m/W, η_2 = 5.6931x10^{-19} m^2/W, χ^3 = 2.9491x10^{-13} esu) of the 3NACL material was statutory evaluated by Z-scan studied. Here, β and η_2 are positive value due to the saturated absorption and self-focusing effect was observed in open and closed aperture z-scan curve. Above all these findings 3NACL was suitable material for NLO and optoelectronic applications.

1. Introduction

Current technological era, experimenters gave high importance to synthesis the new third-order nonlinear optical crystals, because of their applications in the field of optoelectronics and photonics [1].These optical materials become more important because of their multi-mode potential demand of signal process, optical logic gates, optical data storage and photo electronic devices [2, 3]. The third-order nonlinear optical susceptibility value especially it's real and imaginary part value plays a crucial function to design optical device like optical switching, optical limiters, etc., [4]. When comparing to the inorganic crystals, organic crystals are ease to design, light weight, low cost, Low dielectric constant and having exceptional optical and marvellous NLO responses [5–7]. Both solid and solute state ortho, meta and pare di substituted benzene ring derivatives expressed high nonlinear optical properties [8]. Nitroaniline is one of the di substituted benzene ring derivative. Generally, Nitroaniline group compounds are belonging to the push and pull type molecules. It has one electron rich donor amino group and one electron deficient acceptor nitro group connected by a conjugated π electron system. So, intramolecular charge transfer was occurred in Nitroaniline compounds. Due to the intramolecular charge transfer, Nitroaniline compounds are exhibit perceptible NLO and optoelectronic effect. These substances can be used to laser light, optical computing, high speed data processing and optical telecommunication system [9]. This statement motivates us to grown the organic donor acceptor type Nitroaniline chemical group crystal and to study their unique properties. In the present work we focus to survey the physicochemical properties of 3-Nitroanilinium chloride (3NACL). As the result we have developed good quality 3NACL single crystal by slow evaporation technique. Then the grown crystal was subjected to various characterization studied. As

a result, 3NACL single crystals are optically high transparency, thermally stable, good mechanical stability, valuable dielectric response and exceptional higher order nonlinear optical response. Above all findings concluded that, synthesised 3NACL single crystal material is a marvellous candidate for NLO and optoelectronic applications.

2. Experimental Details

The single crystal of 3NACL was synthesised by equimolar ratio (1:1) of AR grade 3- Nitroaniline and hydrochloric acid in ethanol solution. The reaction mechanism of the 3NACL is depicted in Fig. 1. The initial materials are taken in a beaker and stirred at room temperature. After four hours stirring, it reached homogeneous temperature and concentration. Then the resultant solution was filtered using Whatmann filter paper. Filtered solution was taken in a beaker and covered with thick aluminium foil. Then the beaker was kept undisturbed and to allow the slow evaporation process. After 22 days, 6×3×2 dimension orange colour single crystal of 3NACL was harvested. Figure 2 depicted the single crystal of 3NACL.

3. Results And Discussion

Unit cell parameters and structural details of the laboratory synthesised 3NACL single crystal was determined by Single crystal XRD analysis using Bruker Kappa Apex II Diffractometer. From the XRD result, the synthesised 3NACL crystals are belongs to centrosymmetric space group P1 with triclinic crystal system. The single crystal XRD parameters are a=6.8913Å; b=7.8801Å; c=14.6259Å, α=87.021°, β=81.392°, γ=73.231° and V=761.32 $Å^3$. The procured crystallographic values are in good consensus with the reported structural values are depicted in Table 1[10].

Table 1 XRD result of 3NACL single crystal

Parameter	Reported result [10]	Present result
Empirical formula	$C_6H_7N_2O_2^+.Cl^-$	$C_6H_7N_2O_2^+.Cl^-$
a(Å)	6.9936	6.8913
b(Å)	7.8608	7.8801
c(Å)	14.6708	14.6259
α≠ β≠ γ	87.079°≠81.813°≠73.597°	87.021°≠81.392°≠73.231°
Volume ($Å^3$)	765.77	761.32
System	triclinic	triclinic
Space group	P1	P1

3.2 FTIR analysis

FTIR analysis was used to identify the function groups present in the compound. Here, Perkin Elmer Spectrum Two FTIR Spectrometer is used to record the FTIR Spectrum of 3NACL. Figure 3 depicted the recorded FTIR Spectrum of 3NACL. From the recorded FTIR spectrum, the N-H asymmetric stretching frequency which almost overlaps with aromatic C-H asymmetric stretching vibration exhibits a band at 3098 cm^{-1} [11]. The overtones and combined bands are noticed in the range 2003-1697 cm^{-1}. The sharp peak was appeared at 1626 cm^{-1} due to the present of N-H bending vibration. NO_2 asymmetric stretching vibration and the corresponding symmetric stretching vibration was observed at 1500 cm^{-1} and 1346 cm^{-1}. The strong peak at 1251 cm^{-1} assigned to NH_3^+ inplane bending vibration. The prominent peak was obtained at 1086 cm^{-1} due to the presence of C-N stretching vibration respectively.

3.3 Hirshfeld surface analysis

The intermolecular interactions of the 3NACL was investigated through Hirshfeld surface (HS) [12] and the associated 2D-fingerprint plot (FP) [13] analysis using Crystal Explorer 3.1 [14]. The cif file of the 3NACL crystal is the input file for the Crystal Explorer 3.1 software. HS mapped with different properties d_e, d_i, d_{norm}, shape index and curvedness are provided the good information for the intermolecular interactions and crystal packing of the 3NACL crystal molecules [15]. Nearest nucleus outside and inside the surface is denoted as d_e and d_i. In the HS analysis, the red region denotes the negative d_{norm} value (closer intermolecular interactions) and blue region denotes the positive d_{norm} value (longer intermolecular interactions). The dominant H…H interaction in the title compound is noticeable as a dark red spot in d_{norm}, while the dim red spot is due to Cl—H…O interaction. The Hirshfeld surfaces of 3NACL molecule are depicted in Fig. 4.

Plotting between d_i versus d_e was gave the two dimensional fingerprint plot, reproduced from the Hirshfeld surface, which conclude the intermolecular contacts. The overall 2D-fingerprint plot for the 3NACL and those attributed into H…H, Cl…H/H…Cl and C…O/O…C interaction were depicted in Fig. 5. From the fingerprint plot H…H & H…Cl interactions are strong and C…C interaction is very low in 3NACL molecule. Especially H…H interaction is above 40%. Due to the high hydrogen bond interaction 3NACL molecules are brilliant candidate for NLO and optoelectronic device fabrications.

3.4 UV- Visible analysis

Perkin Elmer Lambda 35 UV-Visible spectrometer is an instrument used to record the UV-Visible spectrum. Recorded UV-Visible spectrum of the 3NACL crystal is used to study the optical behaviour of the crystal. From the transmittance spectrum (Fig. 6) the cut of wavelength is 276nm due to the intramolecular charge transfer between the electron rich donor amine group to the electron deficient acceptor nitro group. The grown crystal exhibits 83% transmittance depicted its excellent transparency, purity and structural perfection.

Due to the intra molecular charge transfer and high transmittance 3NACL crystals are used to fabricate NLO and optoelectronic device.

The graph was plotting between direct band gap $(\alpha h\nu)^2$ vs. Photon energy (hv) gives the optical band gap energy of the 3NACL single crystal as depicted in Fig. 7. Then the linear region of the curve was extra plotting to the x axis (photon energy) [16]. Here, the band gap energy of the 3NACL crystal is 4.5 eV. So, the single crystal of 3NACL is suitable material for optoelectronic device fabrications [17].

3.5 Thermal analysis

The 3NACL powder sample weight 5.38mg was taken in the instrument of Perkin Elmer TG/DTA Thermal analyser to study the thermal properties. The resultant TG/DTA curves of 3NACL is depicted in Fig. 8. From the TG curve, the 3NACL sample was thermally stable up to 110°C. When increasing the heating, the 3NACL was start to decreasing its weight 3.46% from 110°C to 164°C. Further heating, 95.18% of weight loss was obtained at 251°C, which indicates the decomposition point of the 3NACL sample. Finally, only 1.36 of residual mass was obtained at 800°C. In the DTA curve, there are two endothermic peak was obtained. The first peak was obtained at 119°C, which indicates the melting point of the sample and the second peak was obtained at 251°C, which indicates the decomposition point of the 3NACL sample. The sharpness of the endothermic peaks denotes the purity and high crystallinity of the 3NACL single crystal. Especially, the decomposition point of the DTA curve was perfectly coincide with the TG curve, and there is no phase transition till the sample get melt, which informs 3NACL crystal was excellent candidate for NLO application up to the limiting of 110°C.

3.6 Vickers microhardness analysis

Shimadzu HMV-2T Vickers microhardness testing device is an instrument used to estimate the mechanical property of the 3NACL single crystal. Mechanical properties of the crystals play the dominant role in fabrication of the optical and electrical devices. Figure 9a depicted the plot between hardness number H_V and load P. From the plot, the hardness number increases with applied load due to the reverse indentation size effect (RISE) [18]. The work hardness coefficient (n) of 3NACL material was calculated by plotting a graph between log P& d and the slope drawn, it gives the n value as 2.73(Fig. 9b). The work hardness coefficient value is above 2, so the 3NACL single crystal belongs to the soft material according to Onitsch [19] statement.

The mechanical property of synthesised 3NACL crystal, such as Yield strength (σ_y), Elastic stiffness constant (C_{11}), fracture toughness (K_c) and Brittleness index (B_i) were calculated [20] in Table 2 for different loads and their respected plots were drawn as depicted in Fig. 10 (a, b, c & d) respectively. In the Elastic stiffness graph (Fig. 10b), it is noticed that the C_{11} increases with increase in load, which specifies that the binding of the neighbouring atoms are very strong.

In the fracture toughness graph (Fig. 10c), it inspected that fracture toughness increases with load increases, which designated that the grown 3NACL crystal has good mechanical stability. From the Fig. 10d, it is monitored that B_i decreases with increasing the applied load, which stipulated that 3NACL is

suitable for various device fabrications. Hence, laboratory synthesis 3NACL single crystals are mechanically stable and acceptable for different NLO material device fabrications

Table 2 Mechanical parameters of grown 3NACL crystal

Load P (g)	H_V (Kg/mm^2)	σ_y (GPa)	C_{11} (×10^5 GPa)	K_c (×10^4 Kgm$^{-3/2}$)	B_i (m$^{-1/2}$)
25	52.3	11.14	10.17	3.13	167.09
50	65	13.85	14.88	6.25	103.94
100	93.35	19.87	28.03	12.50	74.68

3.7 Dielectric studies

LCR impedance analyser is an instrument used to examine the electrical property of the synthesised 3NACL single crystal in the frequency range of 1 KHz to 2 MHz and different temperature at 333K, 353K and 373K. Figure 11(a) & 11(b) was depicted the graph plotting between the dielectric constant (ε_r) and dielectric loss (tanδ) of the grown 3NACL crystal with log frequency at different temperature. From the Fig. 11a, it is seen that the dielectric constant is relatively high in the lower frequency region, due to the contribution of space charge polarization. It is clear from Fig. 10b that the Dielectric loss (tanδ) should be maintained as low as possible in the higher frequency region, while the material was probable applicant for NLO and micro-electrical device applications [21]. In the Fig. 11c depicted the plot between the ac conductivity (σ_{ac}) and log frequency of 3NACL material. From the ac conductivity graph, it is noticed that ac conductivity increases with applied frequency increases, which designated that the grown 3NACL crystal was suitable material for fabrication of optoelectronic devices.

Dielectric solid state parameters

The Dielectric solid state parameters play an important role in the fabrication of electronic device industries. Here, the theoretical parameters such as Plasma energy $h\omega_p$ (eV), Penn gap energy E_P(eV), Fermi energy E_F(eV), Electronic polarizability α (cm^3) were estimated [22] and the resultant values were tabulated (Table 3) for the 3NACL material. The good value of polarizability forecasts that the 3NACL material was felicitous candidate for the electronic device fabrications.

Table 3 Dielectric solid state parameters of 3NACL crystal

Parameters	Values
Plasma energy $h\omega_p$ (eV)	20.77
Penn gap energy E_P(eV)	4.65
Fermi energy E_F(eV)	16.83
Electronic polarizability (α) using Penn analysis (cm^3)	3.93×10^{-23}
Electronic polarizability (α) using Clausius-Mossotti equation (cm^3)	4.11×10^{-23}

3.8 Laser damage threshold study

Now a day's laser and the technologies play a prominent role in multi-mode application. Laser damage threshold (LDT) is one of the laser technology studies to inspect the surface tolerance of crystal under the laser beam. This surface tolerance capacity of the 3NACL was inspected by using Q-switched Nd: YAG laser (wavelength=1064nm, pulse width=6ns, repetition rate=10 Hz). Optical microscope image of laser damage surface part of the 3NACL single crystal was shown in Fig. 12. The LDT value was calculated using the relation, Power density $P_d = E/\tau A$ GW/cm^2, where E is the energy (mJ), τ is the pulse width (ns) and A is the area of the circular spot (cm^2) [23]. The calculated LDT value of the 3NACL crystal was 4.3 GW/cm^2. The higher value of the LDT value indicates that the grown material was brilliant candidate for laser weapon fabrication.

Z-scan study was used to examine the third-order NLO property of the materials. Generally, centrosymmetric crystals are not obeyed the second-order NLO property. It only obeys the third-order NLO property. 3NACL single crystals having centrosymmetric space group P1 from the XRD analysis. In this situation, the title compound only obeys the third-order NLO property. So, third-order NLO property of the 3NACL was examined by closed and open aperture z-scan technique [24]. Here, 532nm wavelength Nd: YAG laser beam was used. The third-order nonlinear refractive index η_2, nonlinear absorption coefficient (β) and the third-order nonlinear susceptibility (χ^3) of the 3NACL compound in ethanol at 0.5mM concentration and 0.48 GW/m^2 intensities were calculated [25]. In an open aperture curve, laser intensity increased the transmittance also increased. So, β is positive due to the presence of saturation absorption (SA). In closed aperture curve, normalized transmittance was obtained in valley to peak curve. So, η_2 is positive due to the self-focusing. Fig. 13a&13b depicted the open and closed aperture plot of 3NACL crystal respectively. Finally, estimated third order nonlinear optical parameters are reported in Table 4. From the obtained results, 3NACL crystals are promising candidate for photo sensors and all third-order nonlinear optical application.

Table 4 Third order NLO parameters of 3NACL sample

Third-order NLO parameters	values
Nonlinear refractive index (η_2)	5.6931($x10^{-19}$) (m^2/W)
Nonlinear absorption coefficient (β)	7.5472($x10^{-12}$) (m/W)
Real part of the third-order susceptibility [Re χ^3]	2.6411 ($x10^{-13}$) (esu)
Imaginary part of the third-order susceptibility [Im χ^3]	1.3121 ($x10^{-13}$) (esu)
Third-order nonlinear optical susceptibility [χ^3]	2.9491($x10^{-13}$) (esu)

4. Conclusion

Potentially new organic single crystal of 3NACL was synthesised by slow evaporation technique with the empirical formula as $C_6H_7N_2O_2^+.Cl^-$ and the system is triclinic with space group as P1. The Hirshfeld surfaces and two dimensional fingerprint plot analysis elucidated that hydrogen bond interaction is more dominant in the title compound, so 3NACL crystals are used to make optoelectronic devices. The cut-off wavelength and optical band gap energy was calculate from UV–Vis analysis and the values are 276nm and 4.5eV. The TG/DTA analysis revealed the title compound was stable up to 110°C and decomposition point (251°C) of the TG curve was perfectly coincide with the DTA curve. The work hardness coefficient value was greater than 2 (n=2.73), so 3NACL single crystals are soft material nature. LDT studies revealed that the synthesis material was able candidate to make a laser weapons. Dielectric studies revealed that the grown crystals are exhibit acceptable dielectric response. From z-scan studies, β is positive due to the saturated absorption and η_2 also positive due to self-focusing was observed in open and closed aperture curve respectively. Above all these results are declared that the 2NABR single crystal might to be auspicious candidate for nonlinear and optoelectronic applications.

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Figures

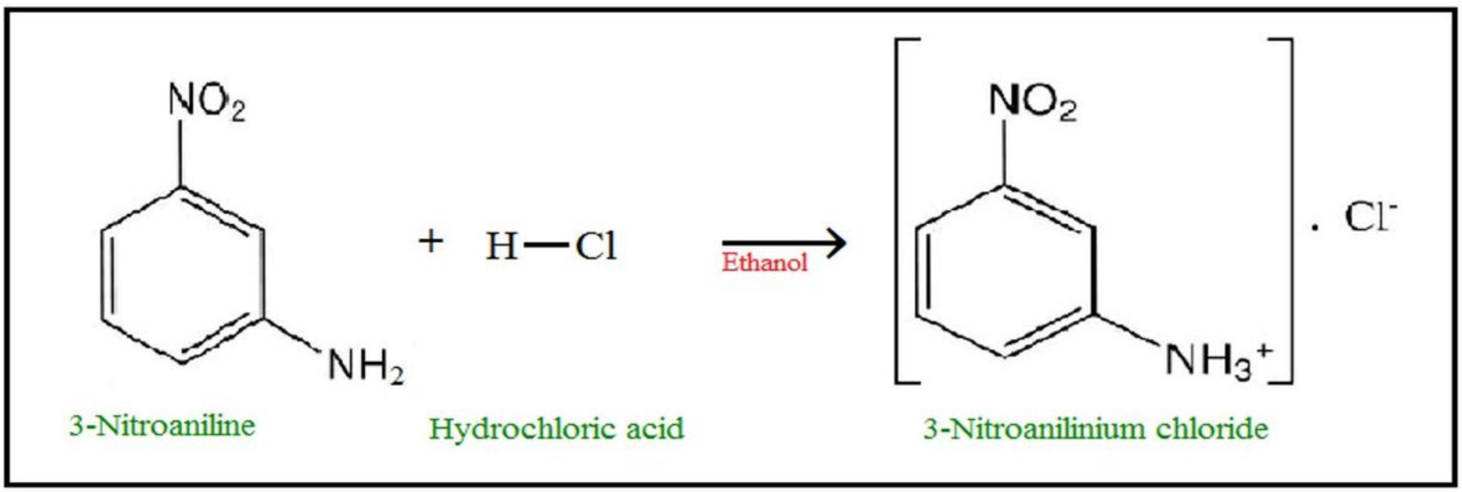

Figure 1

Reaction mechanism of 3NACL

Figure 2

single crystals of 3NACL

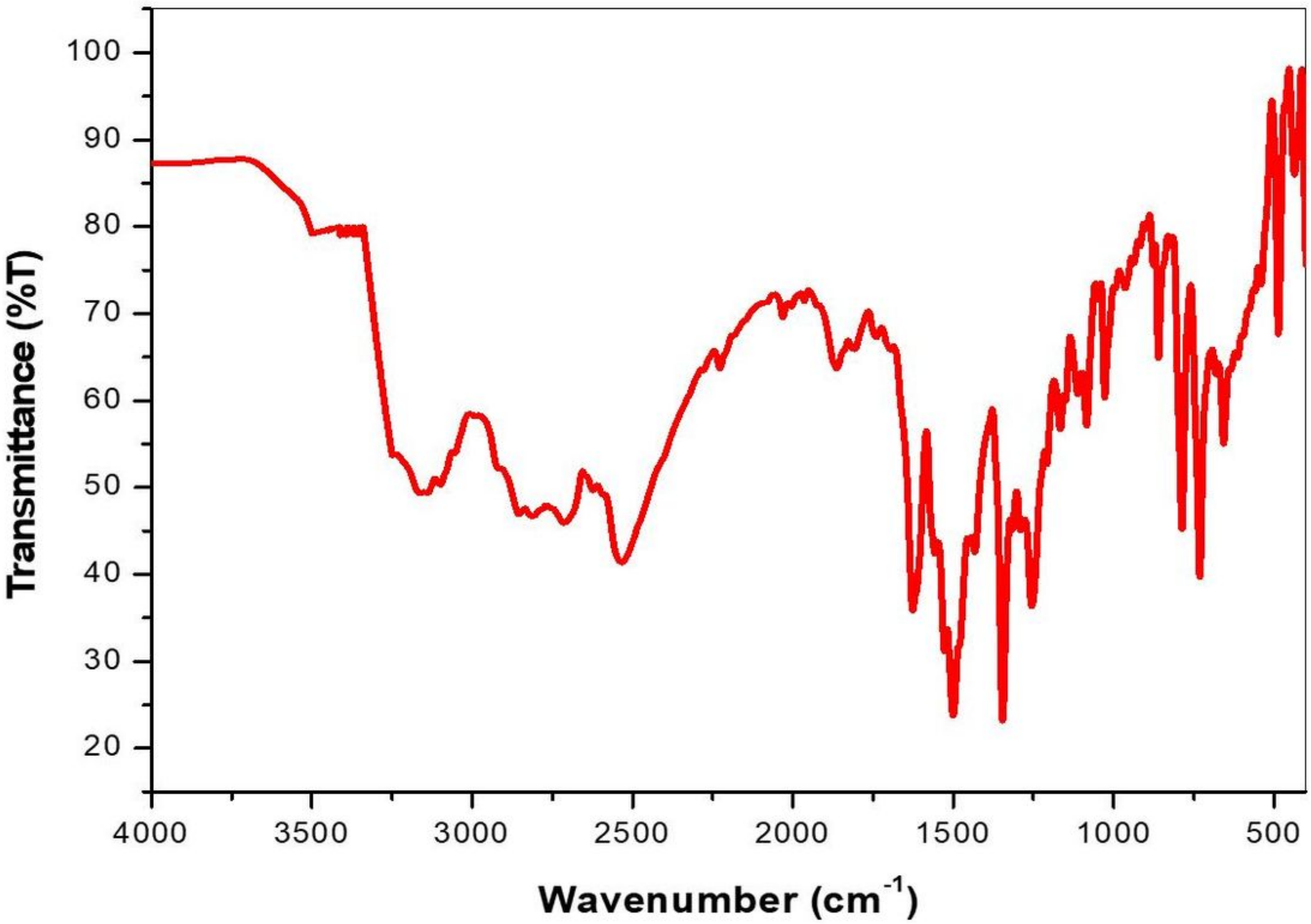

Figure 3

FTIR spectrum of 3NACL

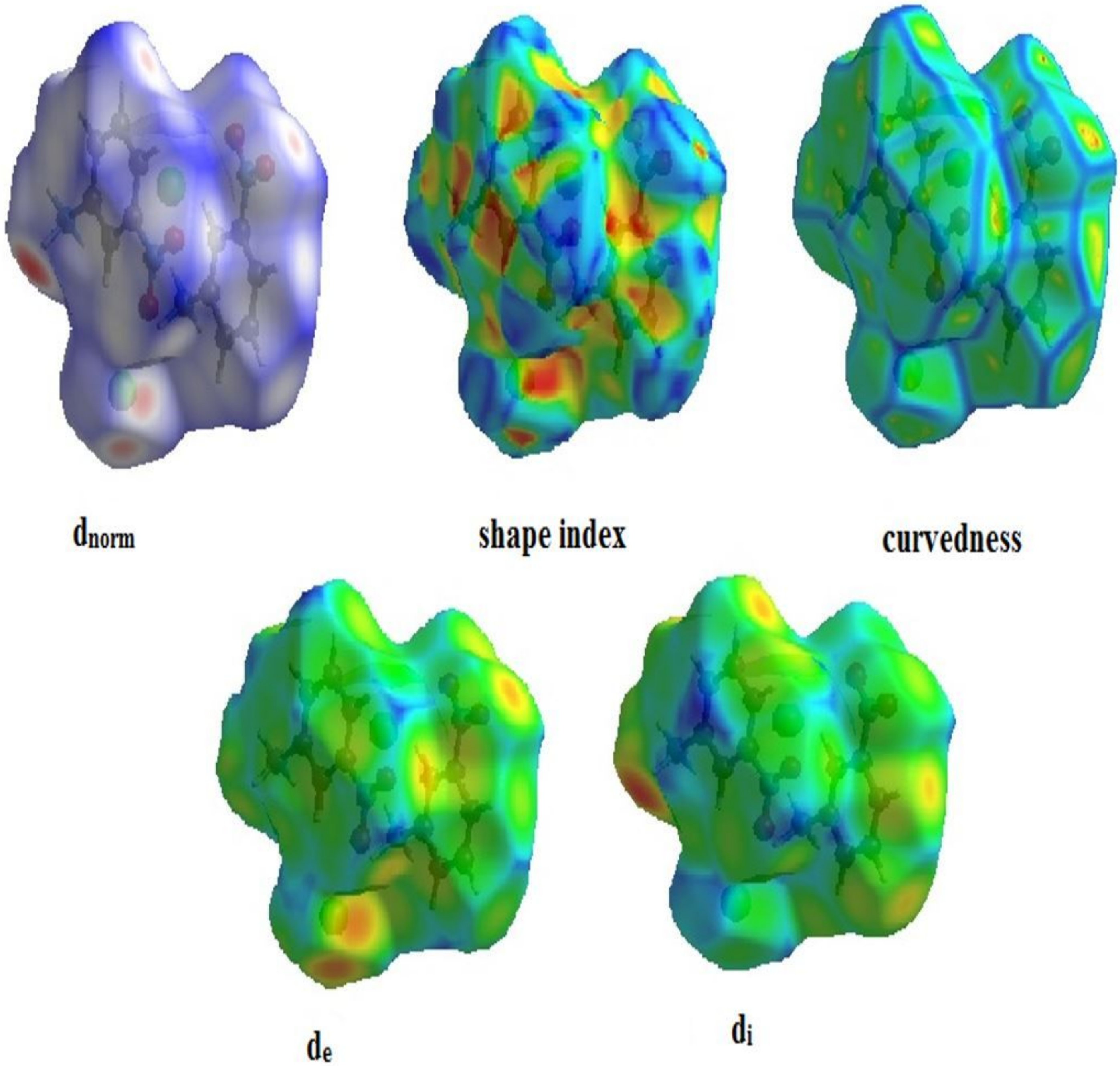

Figure 4

Hirshfeld surfaces of the molecule 3NACL

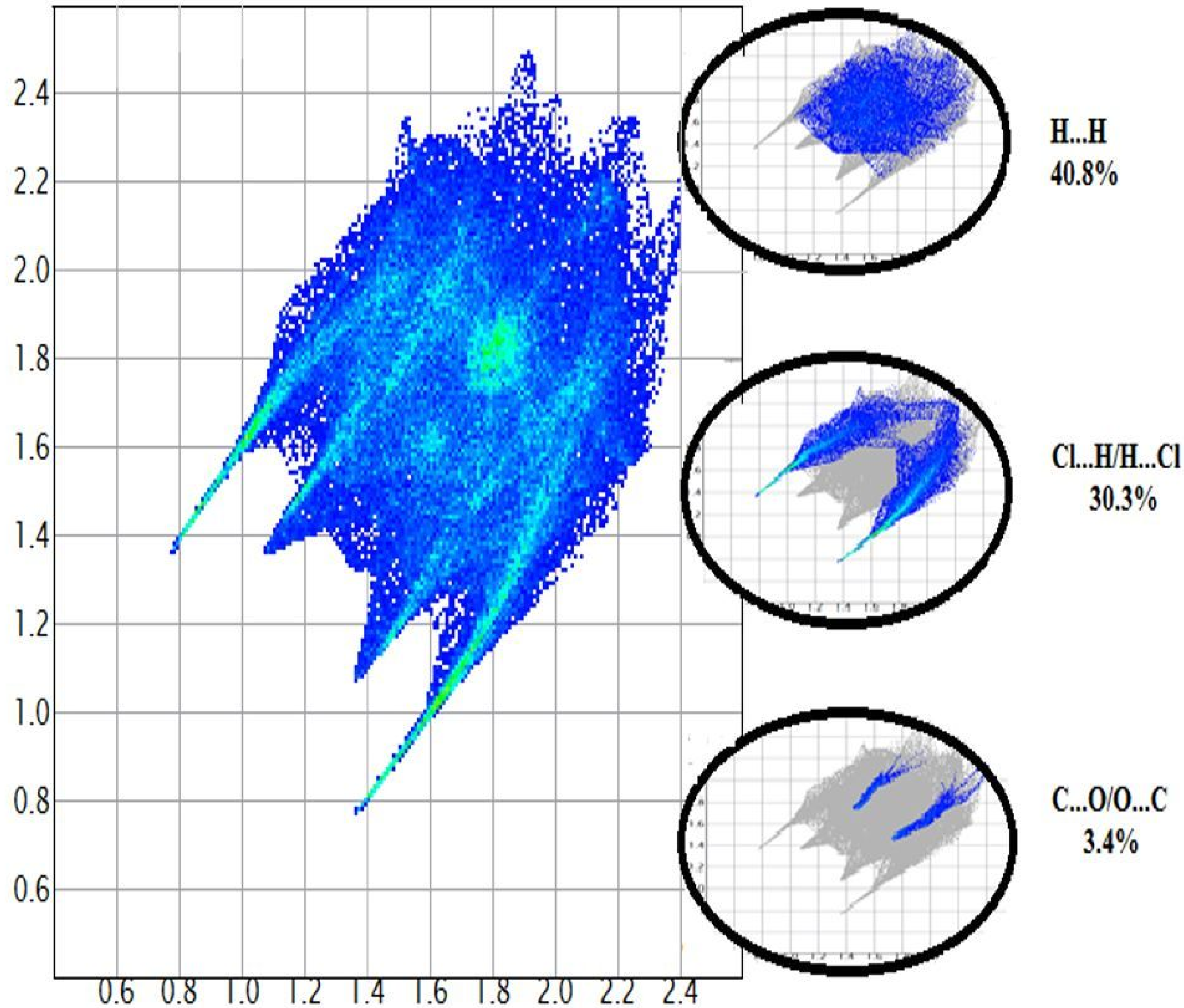

Figure 5

Total Fingerprint plot with H...H, Br...H and C...O interactions of the 3NACL molecule

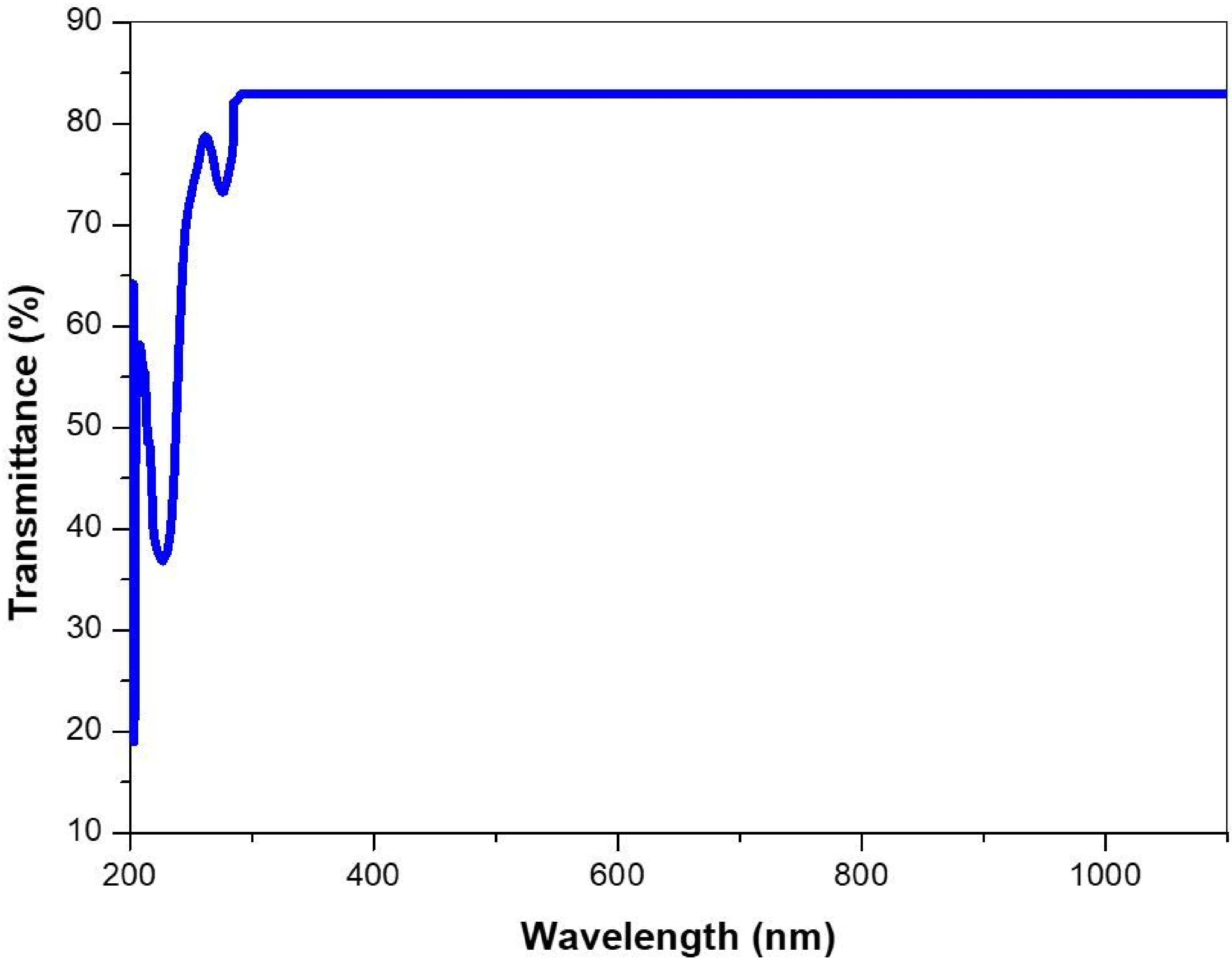

Figure 6

UV-Vis transmittance spectrum of 3NACL

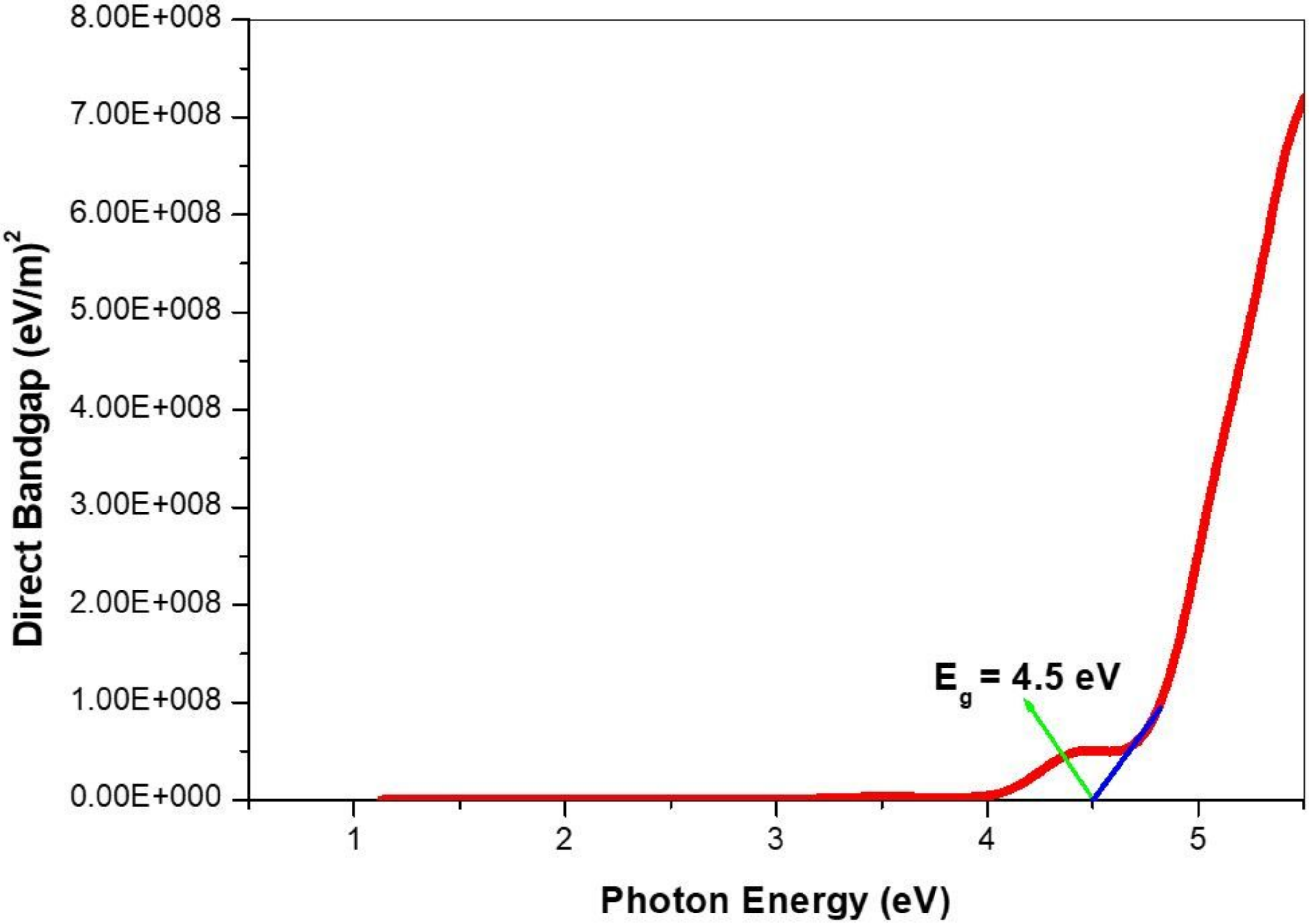

Figure 7

Variation of direct Band gap vs. photon energy

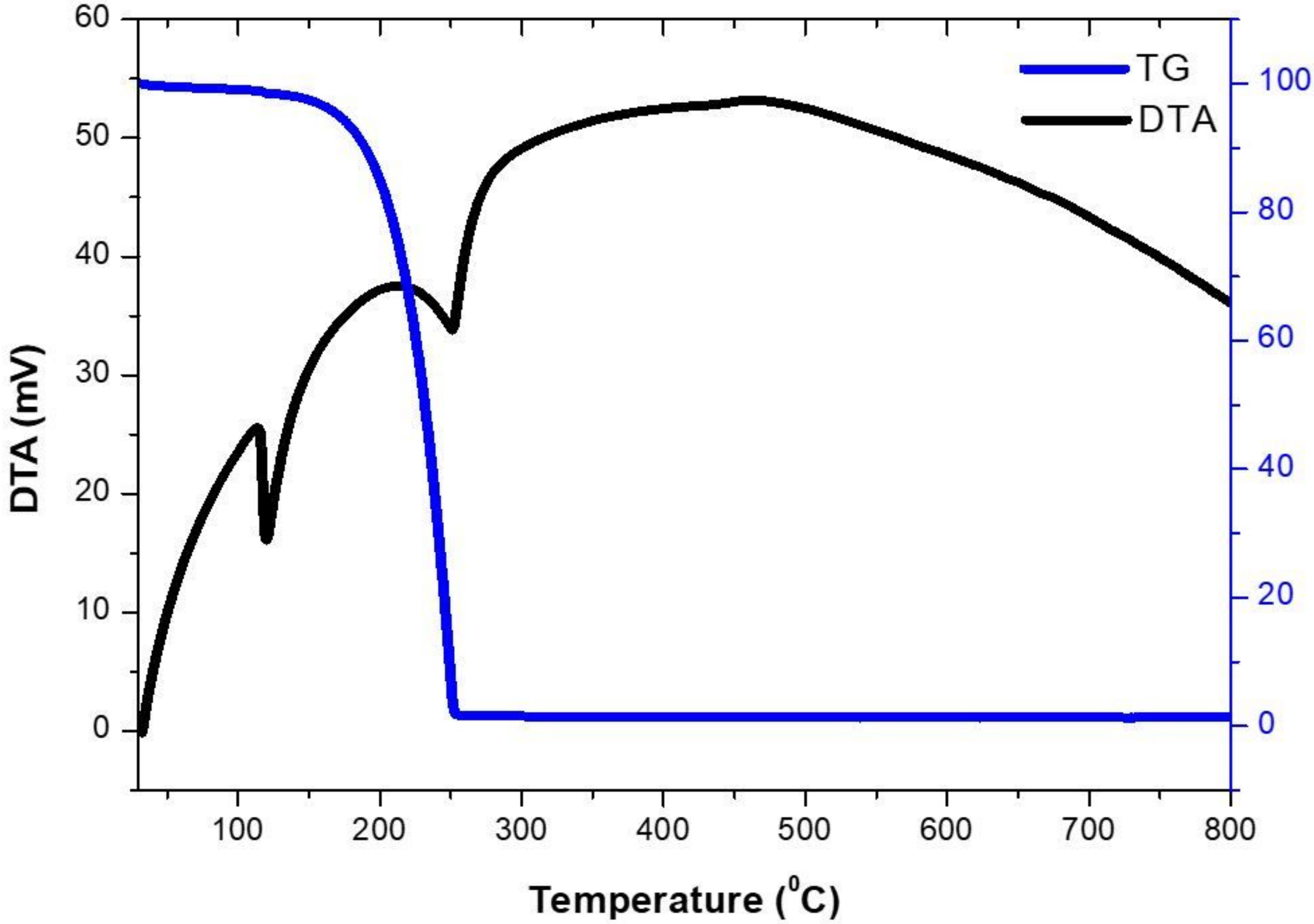

Figure 8

TG-DTA thermogram of 3NACL crystal

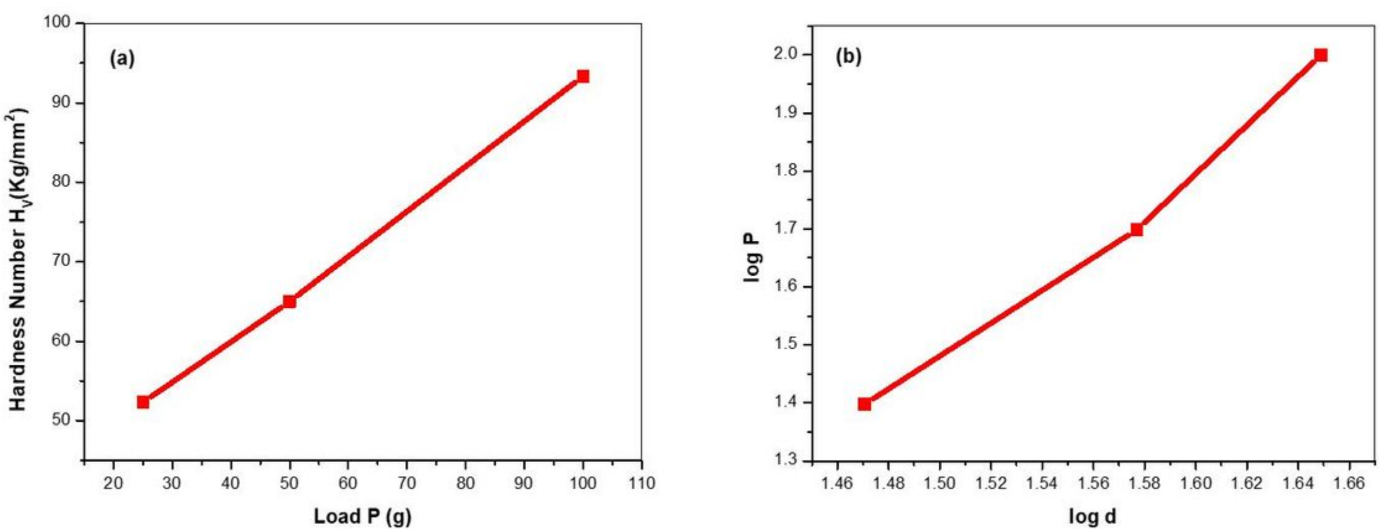

Figure 9

a Hardness number vs. load P b log P vs. log d for 3NACL crystal

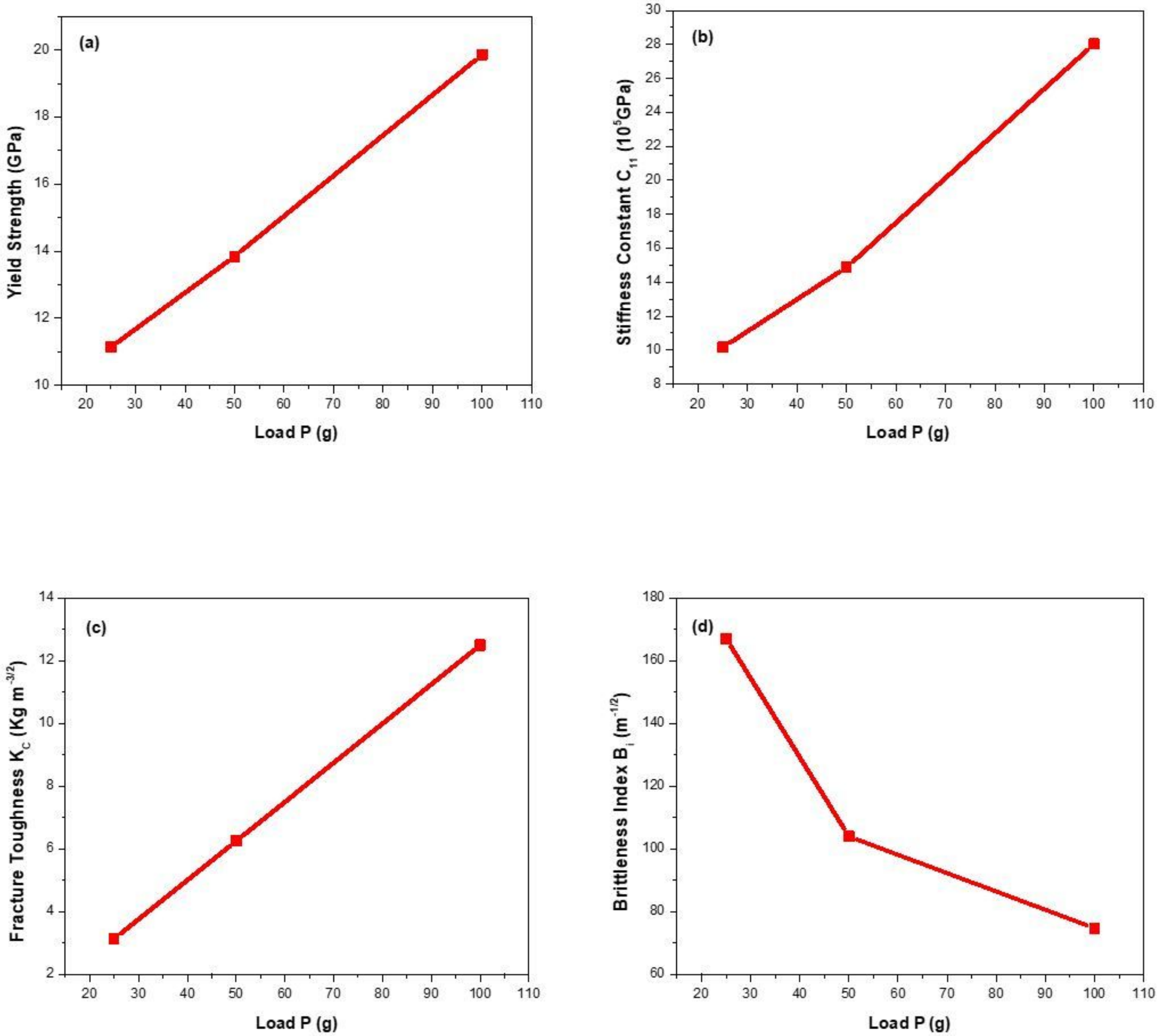

Figure 10

Variation of a Yield strength b Stiffness constant c Fracture toughness d Brittleness index with applied load of 3NACL single crystal

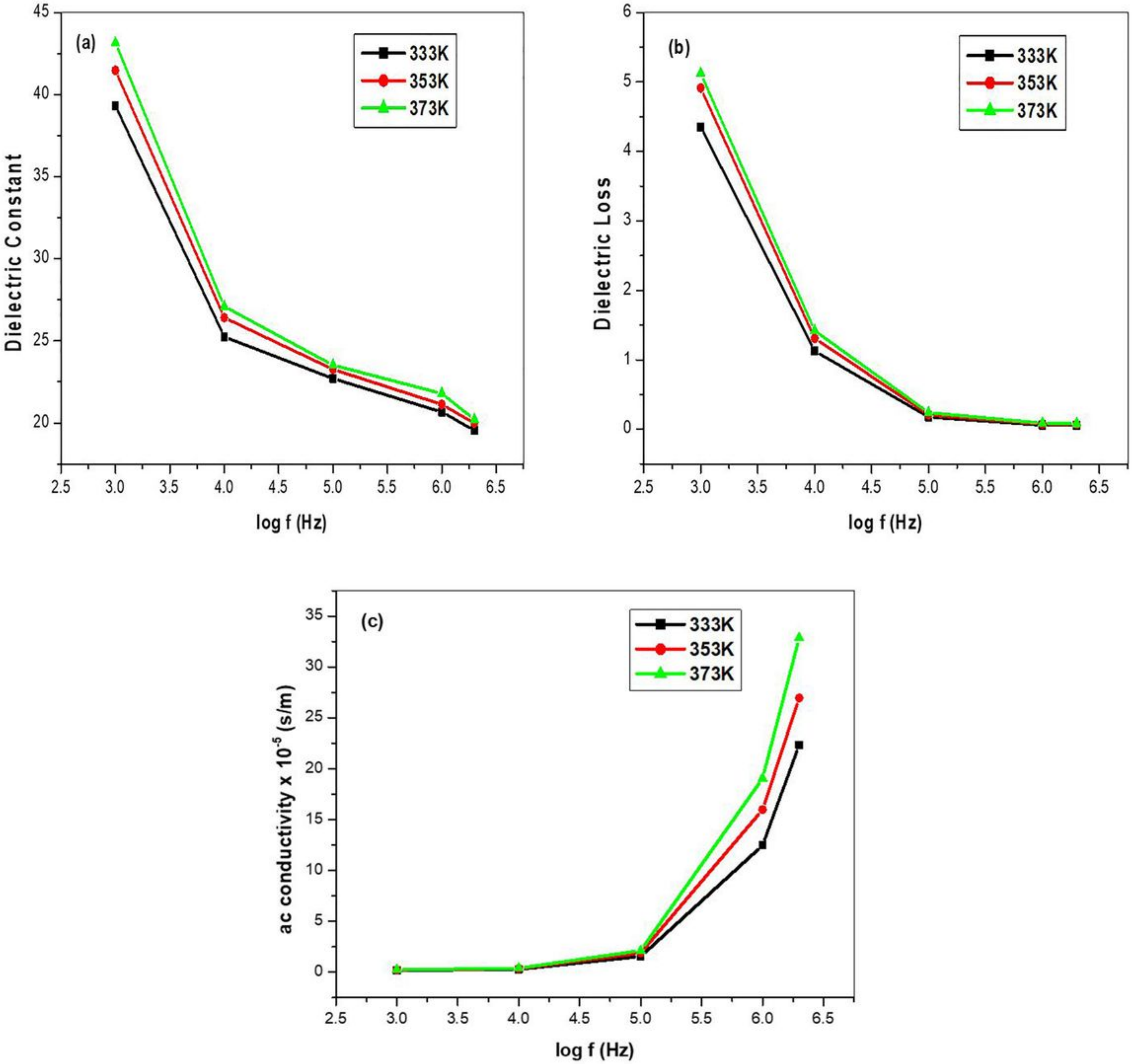

Figure 11

Variation of a dielectric constant b dielectric loss c ac conductivity with log frequency in 3NACL crystal

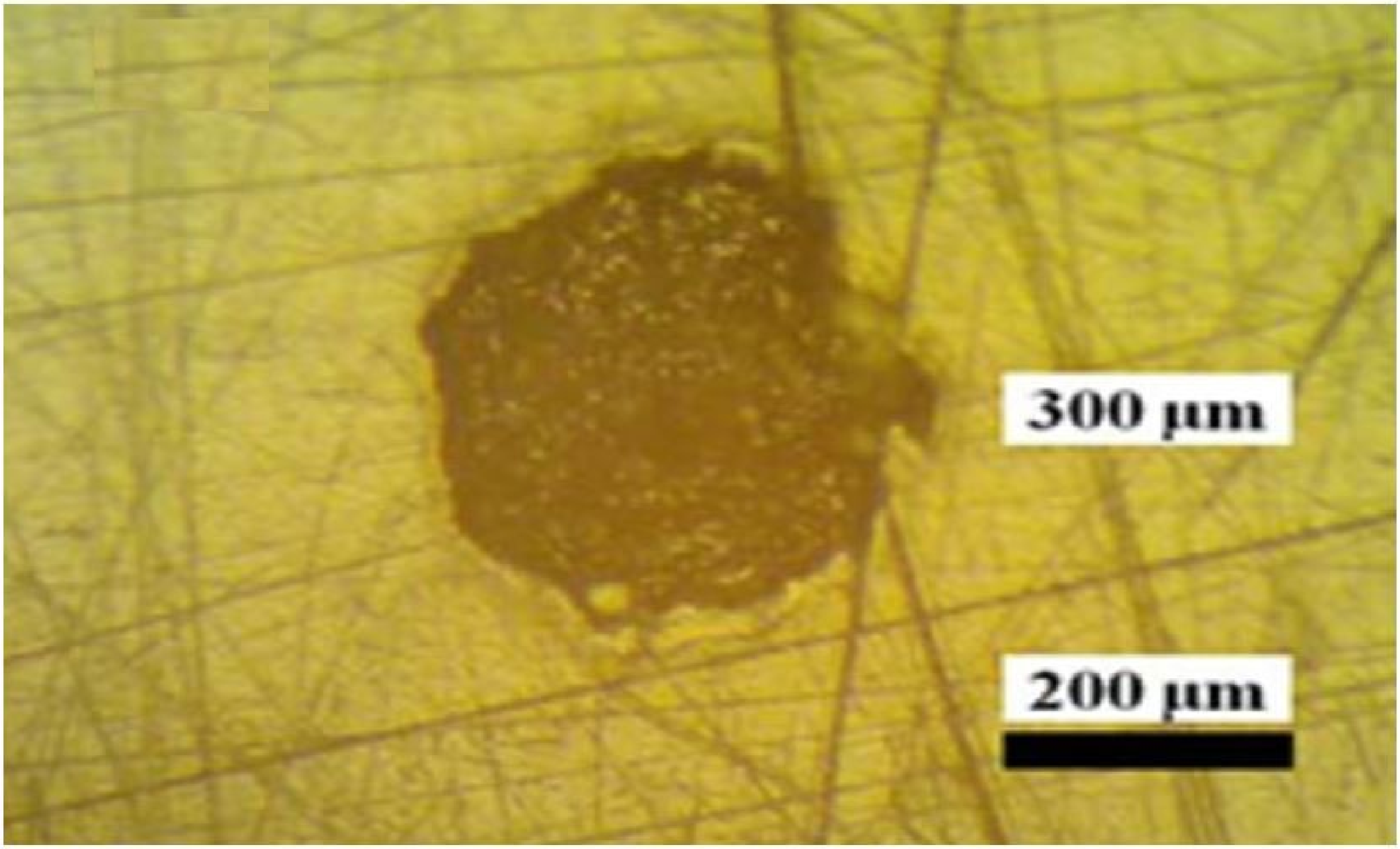

Figure 12

Laser damage surface part of the 3NACL crystal

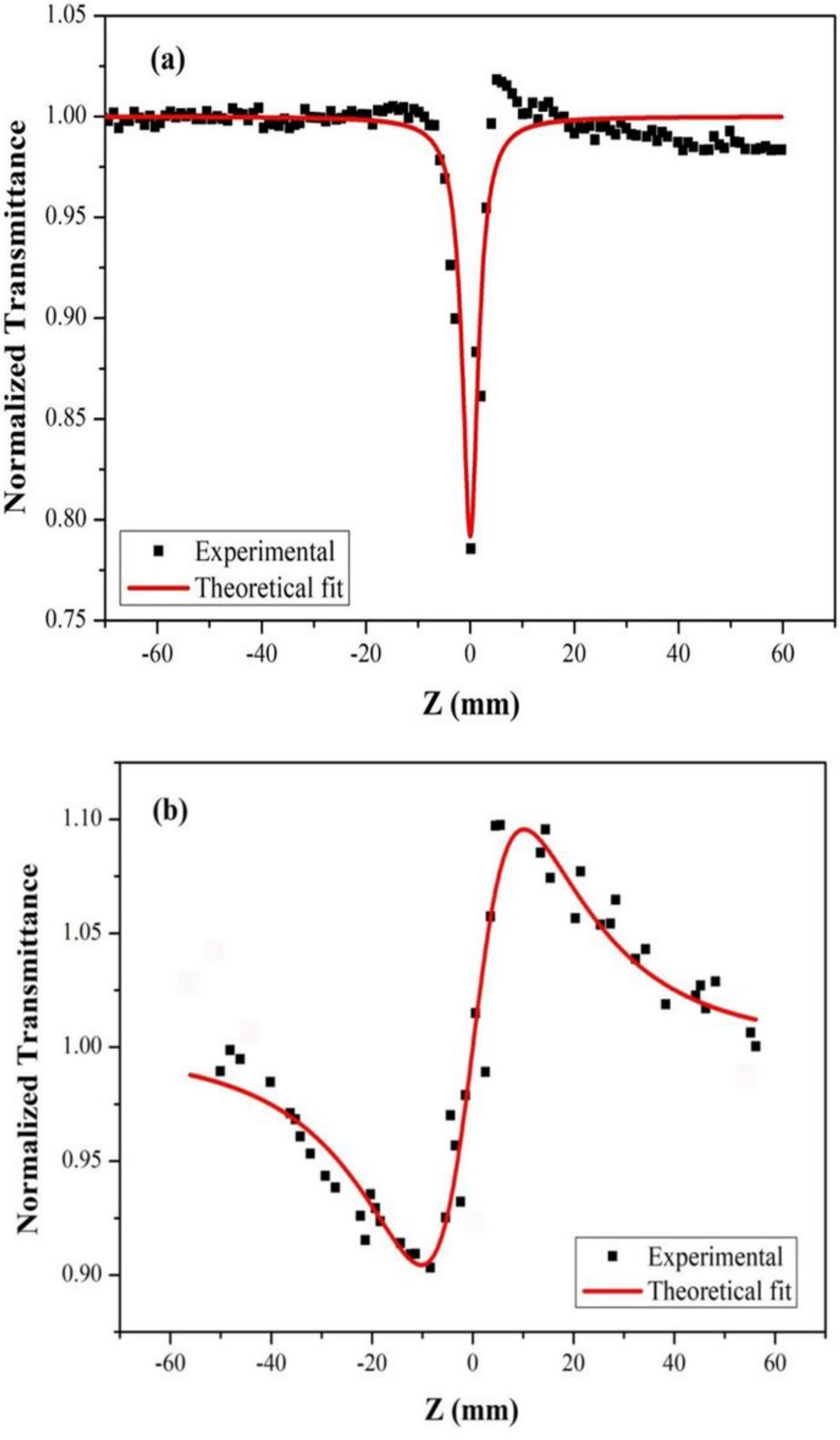

Figure 13

(a) open aperture, (b) closed aperture z-scan plot of 3NACL crystal