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Synthesis, growth, optical, mechanical, thermal and surface studies of ligand based single crystal of tri-allylthiourea cadmium chloride (ATCC)

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ABSTRACT

Metal-organic coordination complex crystal ATCC has been synthesized by slow evaporation technique. The grown crystal was characterized by single crystal XRD technique to determine the cell parameters. The second harmonic generation (SHG) measurement confirms that the ATCC has nonlinear optical property. The UV-VIS-NIR spectroscopic studies revealed that the grown crystal has good optical transparency. The functional groups have been identified using FT-IR spectrum. The mechanical strength of the grown crystal was found from Vickers micro hardness measurement and the thermal stabilities were determined with the aid of thermo gravimetric analysis (TGA) and differential thermal analysis (DTA). The surface morphology was studied by using scanning electron microscope (SEM) and atomic force microscopy (AFM).

INTRODUCTION

Nonlinear optical (NLO) materials find extensive optoelectronic applications such as optical frequency conversion, optical data storage and optical switches in the initially confined laser fusion systems. Incorporation of metals into organic ligand gives a new dimension of study. An important aspect of utilizing these materials for nonlinear optics is their unique charge transfer transitions either from metal to ligand or from ligand to metal. Due to this, in semiorganic materials, the metal – ligand bonding is expected to display large molecular hyperpolarizability, because of the transfer of electron density between the metal atom and the conjucated ligand system. The metal–organic coordination compounds as NLO materials have attracted much more attention for their considerable high NLO coefficients (contrast to inorganic materials), stable physico-chemical properties and better mechanical intension (contrast to organic materials) [1,2]. With the guidance of this theory, many metal–organic coordination materials with good NLO effect have been designed and synthesized. Based on the double – radical structural model, a series of efficient metal organic complex ATMX (AT = allylthiourea M = Cd or Hg, X = Cl or Br) crystals (such as ATCC, ATMC, ATCB and ATMB) in which AT acts as double ligand have been reported. These ligands and their metal (group IIB) complexes are always colourless. Potential NLO materials like bis(thiourea) cadmium chloride (BTCC) and triallylthiourea cadmium chloride (ATCC) are examples of this approach. The structure radical of the organometallic complex, especially in allylthiourea is no longer planar as the benzyl ring, hence the anisotropy of the crystal is reduced as compared with organic crystals. These materials have the potential for combining the high optical nonlinearity and chemical flexibility of organics with excellent transmittance of inorganics.

Allylthiourea complexes have relatively large NLO co-efficient and excellent UV cut-off wavelengths. Among them, the semiorganic crystal triallylthiourea cadmium chloride (ATCC) reported by Zhang and co-workers to has good damage thresholds, relatively high nonlinear coefficients, and very good mechanical stability [3]. The comparatively high optical nonlinearity comes from the distortion of the tetrahedron, which is composed of three AT

and one Cl or Br combining with the metal atoms Cd^{2+} or Hg^{2+}. The distorted tetrahedron arrangement in the material increases the asymmetric structure and hence contributes to the enhanced NLO activity [4-6].
In the present work, high quality single crystal of ATCC has been grown by slow evaporation solution growth technique and is found to exhibit high mechanical strength. The defects, growth pattern and surface morphology of the grown crystals are studied with the help of scanning electron microscopy (SEM) and atomic force microscopy (AFM). The lattice constants have been determined from powder X- ray diffraction (PXRD) method and found that they crystallize in trigonal crystal system. The spectral, optical and thermal properties were studied and the obtained results are being presented here.

MATERIALS AND METHODS

2.1. Material synthesis

Triallylthiourea cadmium chloride was synthesized by taking allylthiourea and cadmium chloride in the ratio of 3:1. The raw materials (AR grade) used in these studies were synthesized in deionized water based on the following reaction:

$$3(CH_2– CHCH_2\ NHCSNH_2) + CdCl_2 \rightarrow [CdCl(CH_2 – CHCH_2\ NHCSNH_2)_3]^+\ Cl^-$$

The purity of the material can be enhanced by repeated recrystallization (typically 2 to 3 times).
Based on solubility data, a known weight of recrystallized powder sample of ATCC single crystal was dissolved in deionized water at temperature 58 ^oC. The solution was constantly stirred for few hours to overcome the concentration gradient in the crystallizer. The pH value played vital role in the crystallization process [7]. The optimum pH value for ATCC was 2.5. The saturated solution was taken in a crystallizing vessel and covered with perforated sheet to initiate slow evaporation at room temperature. Seed crystals were formed due to spontaneous nucleation in the supersaturated solution within 5 days. Optically clear and defect free seed crystals with perfect shapes were chosen for bulk single crystal growth. The seed was suspended in the supersaturated mother solution. Good quality crystals of dimension up to were harvested in a period of 15 to 20 days. The photograph of ATCC crystal is shown in Figure 1.

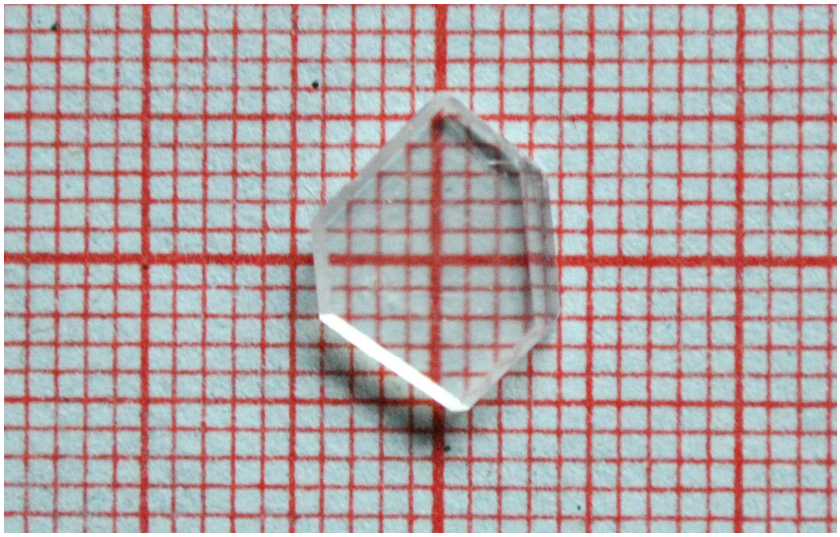

Fig.1. The photograph of ATCC single crystal

RESULTS AND DISCUSSION

3.1. Single crystal X-ray diffraction analysis

It is observed by using Enraf-Nonius CAD4-MV31 single crystal X-ray diffractometer that the grown crystal belongs to trigonal system. The calculated lattice parameters are given in Table 1. These data of the present work is in good agreement with the reported work [6,7].

Table.1. Single crystal XRD data

Crystal Name	Empirical Formula	Crystal System	a (Å)	b (Å)	c (Å)	α (deg)	β (deg)	γ (deg)	Volume $(Å)^3$
ATCC	$CdCl(CH_2 – CHCH_2 NHCSNH_2)_3$	Trigonal	11.43	11.43	28.00	90	90	120	3184

3.2. Powder X- ray diffraction analysis

Powder XRD pattern of the crystalline powder sample of ATCC has been recorded and shown in Figure (2) and various planes of reflection are identified. The sharp peak found in the spectrum shows the better crystallinity. The determined unit cell parameters are compared with single crystal X-ray diffraction results and are in good agreement with the reported value [8].

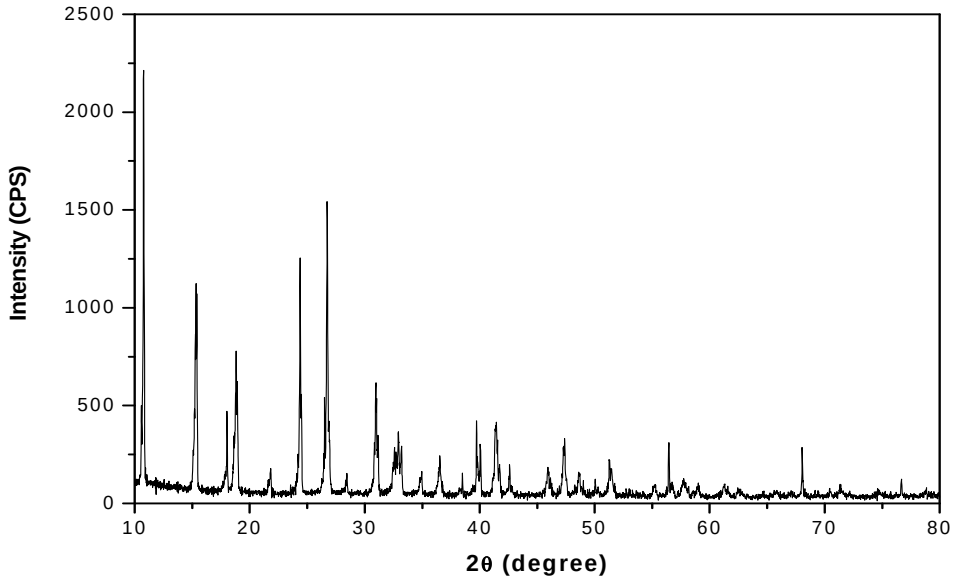

Fig.2. Powder XRD pattern of ATCC crystal

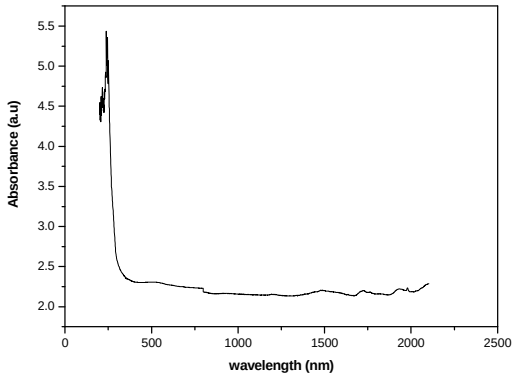

Fig.3(a). UV-absorption spectrum of ATCC crystal

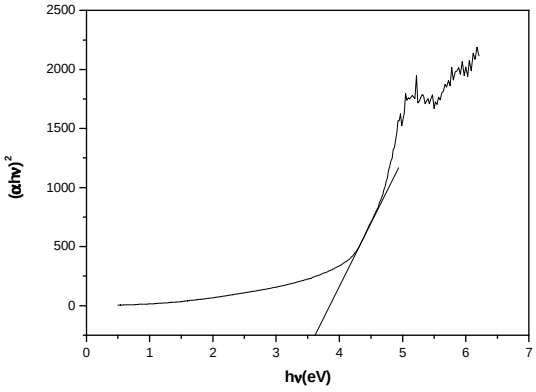

Fig.3(b). Tauc's plot of ATCC crystal

3.3. NLO property studies

The nonlinear optical conversion efficiency test was carried out for the grown crystal using Kurtz powder technique. In this experiment, Q-switched Nd:YAG laser beam of λ = 1064 nm was used. Urea sample powder was used as the reference medium. The second harmonic efficiency was confirmed from the emission of green radiation of

wavelength 532 nm by the crystal. The SHG efficiency of ATCC single crystal is 1.5 times than urea which agrees with the earlier reports [9,10].

3.4. UV-VIS-NIR absorption studies

To know the suitability of ATCC single crystal for optical applications, the UV-VIS-NIR absorption spectra have been recorded in the range of 200-2500 nm covering the entire UV, visible and NIR region. The lower cut-off wavelength for ATCC (Figure 3a) is found to be 291 nm which is matching with the reported value and the absorption is minimum in the region from 300 to 1500 nm. It is well known that an efficient NLO crystal has an optical transparency and lower cut-off wavelength between 200 and 400 nm. The direct optical band gap value of 3.6 eV has been calculated from Tauc's plot (Figure 3b). It is very clear that ATCC has potential prospects for frequency conversion applications [11].

3.5. FT-IR spectral analysis

In order to analyze the synthesized compound qualitatively for the presence of functional groups present in the sample, the FT-IR spectrum was recorded between 400 and 4000 cm^{-1}. The sharp peak is at 1561 cm^{-1} (Figure 4) which corresponds to ν(CN) stretching frequency and it is shifted to higher wavenumber (18 cm^{-1}) when compared to the corresponding frequency found in pure allylthiourea (1543 cm^{-1}) . In addition to this, the band observed at 769 cm^{-1} is assigned to the bending vibration of C=S group. It confirms that the metal ion (Cd^{2+}) had coordinated only with sulphur that is present in the ligand AT [12]. The main bands and their assignments are listed in Table 2.

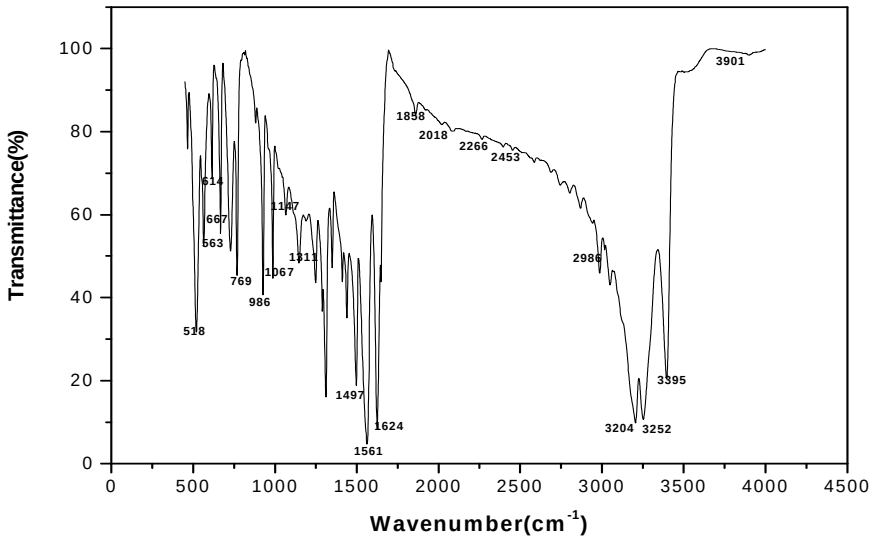

Fig.4. FT-IR spectrum of ATCC crystal

Table.2. Assignments of the main FT-IR band of ATCC

Wavenumber cm^{-1}	Assignment
3395 (s)	$\nu_{as}(NH_2)$
3204 (s)	ν (NH)
1624 (s)	δ (NH_2)
1561 (s)	ν(CN), δ(NCN), ν(C=S)
1497 (m)	ν_{as}(CN)
1311 (m)	δ (NH)
769 (m)	ν (C=S)
563 (s)	τ (CN), π (NH)

3.6. Micro hardness test

The micro hardness studies were carried out on the as grown crystal of ATCC using instrument MUTUTOYO MH 112 (JAPAN) micro hardness tester. To evaluate the Vickers hardness, several indentations were made on the smooth surface of the crystal. Vickers micro hardness number was evaluated from the relation,

$$H_v\,(kg/mm^2) = 1.8544\ p/d^2$$

Where H_v is the Vickers micro hardness number, p is the applied load and d is the average diagonal length of the indentation impression. Dependence of the micro hardness on the load for ATCC crystal has been calculated and shown in Figure (5). The indentation was made on the sample with the load ranging from 50-300 g and the indentation time was kept constant as 10s. The graph indicates that the micro hardness number increases with increasing load [13-16]. At the load above 300 g, micro cracks were observed around the impression and hence, readings were not taken for higher loads. These cracks on the crystal surface due to the release of internal stress generated locally by indentation. The work hardening coefficient value (n) of the grown crystal would be n > 2. Hence, ATCC crystal belongs to soft material.

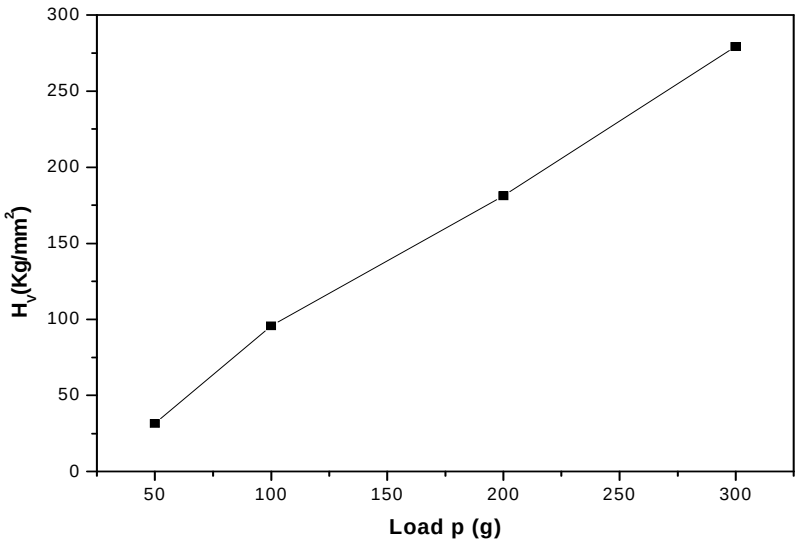

Fig.5. Variation of Vickers hardness number with applied load for ATCC crystal

3.7. Thermal analysis

To study the thermal stability of the crystal, thermo gravimetric (TG) and differential thermal (DTA) analyses were carried out. Figure 6 shows the TG/DTA curves of ATCC crystal. From the TG curve, the thermal stability of the sample is realized up to 200 ^oC and it shows loss in weight due to the molecules, which are loosely bounded to the central metal atom. The change in mass loss confirms decomposition of the sample [17,18]. The percentages of mass loss from 200-260 ^oC and from 260-350 ^oC are 14.69% and 36.76%. The remaining mass (48.55%) appears as residue. The DTA trace shows a sharp endothermic peak at 110 ^oC which is assigned to the melting of the compound. There is another endotherm with the peaks at 215 ^oC and 277.4 ^oC which also indicate the decomposition of the material.

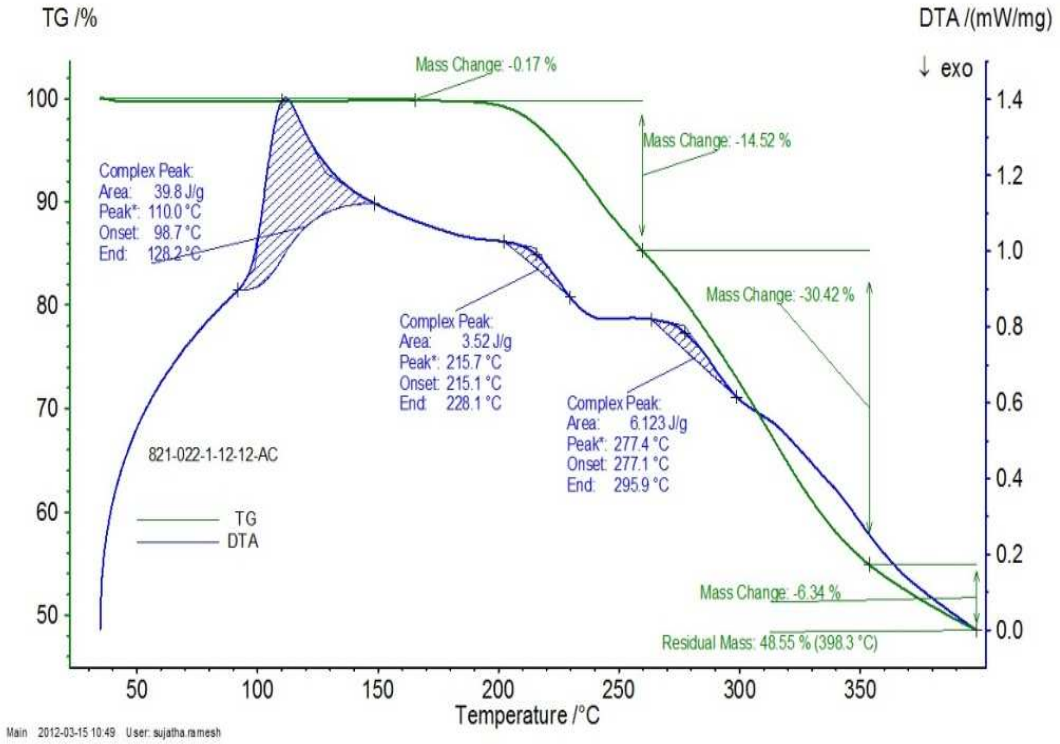

Fig.6. TG-DTA trace of ATCC crystal

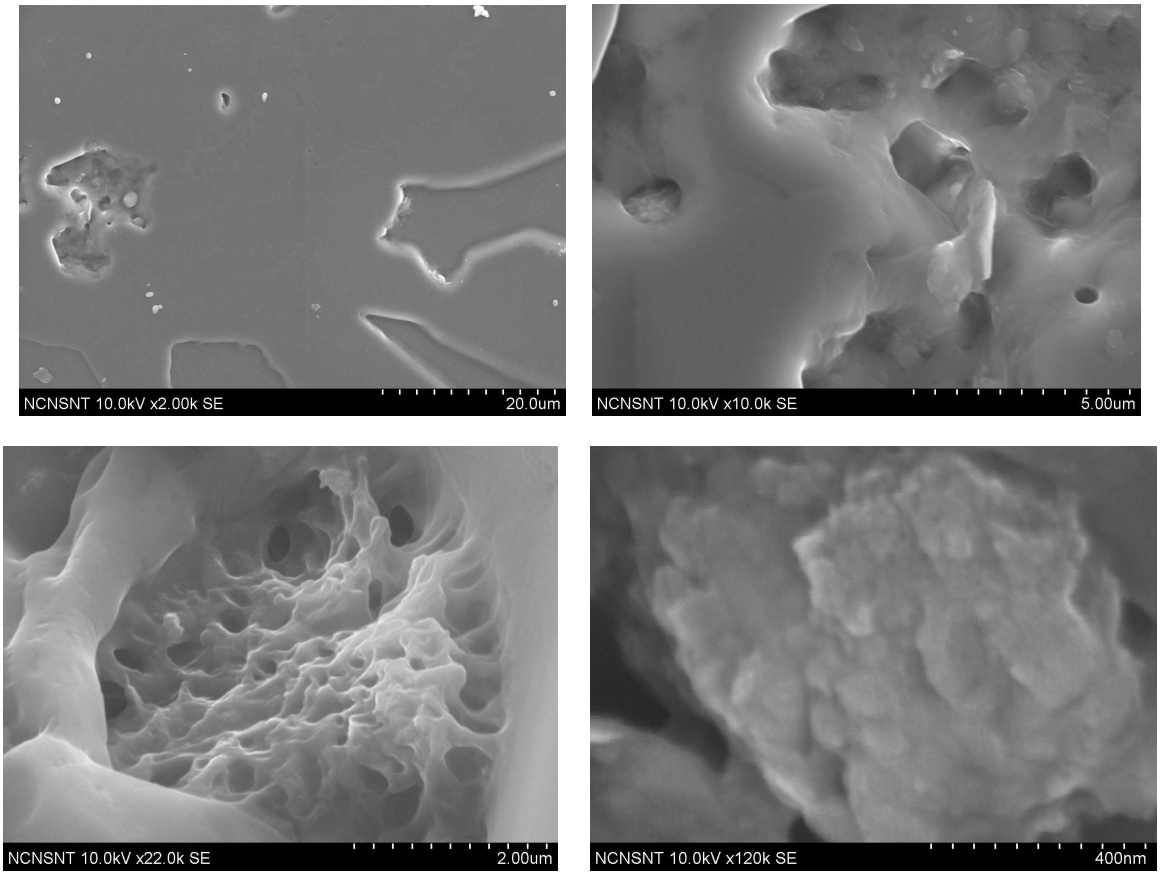

Fig.7. SEM images for ATCC crystal

3.8. Scanning electron microscopy (SEM)

SEM analysis gives information about the nature and suitability for device fabrication and also it is used to check the presence of imperfections. SEM analysis was carried out using SU 6600 field emission scanning electron microscope. Since semi organic crystals are non-conducting in nature gold coating should be done (HITACHI E – 1010 ION SPUTTER) for 10 s before subjecting the ATCC crystal surface to electron beam at different magnifications. Figure (7) shows voids and porous nature. This might be due to solvent inclusions, which is most commonly observed in solution grown crystals [19].

3.9. Atomic force microscopy (AFM) analysis

Atomic force microscopy (AFM) is a relatively new and rapidly advancing technique, proved to be an excellent and unique approach for observing crystal growth dynamics as well as imaging and measuring surface features on a nanometre resolution. Therefore, the advent of AFM has led to a further understanding of the crystal growth as well as the establishment of some new growth theories and models [20]. To collect the three dimensional image for ATCC crystal, PICOSPM 5100 AFM was used and it involves a scanning sharp probe tip (Nanosensors-type; PPP-NCH-50-silicon n+) attached to a cantilever spring across the surface of a solid sample in step mode (non-contact mode). Maintaining a constant force between the probe tip and the sample results in the probe tip going up the "hills" and down into the "valleys" of the sample as the probe tip of radius of curvature < 10 nm is scanned and the corresponding deflections were obtained. Monitoring the movement of the cantilever leads to a high resolution 3-D image of the sample's topography, phase and amplitude. The sample was taken freshly cleaved from the grown ATCC crystal and the surface of the sample was observed in AFM operating in non-contact mode. Figure (8) shows the AFM images of ATCC at different magnifications.

From the 3-D image (Figure 9), the surface of ATCC contains unlike protrusions due to sulphur deposits, less number of peaks and valleys. The surface roughness profile (Table 3) indicates that (S_a = 26.3715 nm) the sample possesses almost smooth surface. The ten-point height (S_z), which is regarded as the difference in height between the average of the five highest peaks and the five lowest valleys along the assessment length of the profile is found to be 245.813 nm. Another parameter, surface kurtosis (S_{ku}) is the measure of surface sharpness. If (S_{ku} >3), the surface is set to have more peaks than valleys.

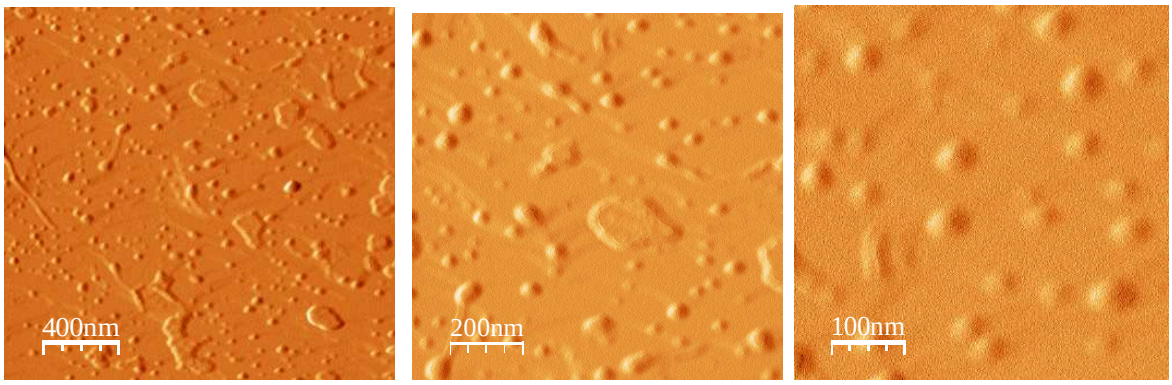

Fig.8. AFM images of ATCC crystal

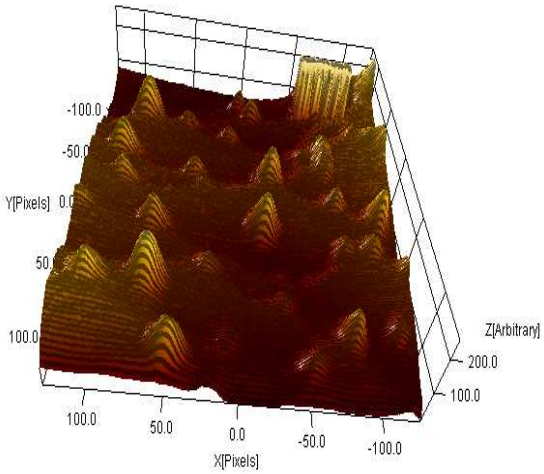

Fig.9. AFM 3-D image of ATCC crystal

Table.3. Surface parameters measured by AFM

Parameter	ATCC
Roughness average (S_a) (nm)	26.3715
Root mean square (S_q) (nm)	33.9597
Surface skewness (S_{sk})	0.864426
Surface kurtosis (S_{ku})	4.74138
Ten-point height (S_z) (nm)	245.813
Density of summits (S_{ds}) (1/µm²)	20992.6

CONCLUSION

A potential semi organic material for second order NLO applications was synthesized and single crystal of triallylthiourea cadmium chloride has been grown by slow evaporation technique. The single crystal X-ray diffraction and powder X-ray diffraction studies confirm the trigonal structure of the grown crystal. The NLO behaviour of the ATCC crystal was observed by Kurtz powder method by the emission of green radiation. The optical studies show that the grown crystal can be used for NLO applications. FT-IR analysis confirms the presence of functional groups in the as grown crystal. Thermal analysis reveals that the ATCC crystal is stable up to 200 ^{o}C. In order to find the mechanical strength of the grown crystal, Vickers micro hardness test was used. SEM and AFM have been employed to investigate the surface and growth morphology of the grown crystal.

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