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RESEARCH ARTICLE

CHARACTERIZATIONS ON SODIUM CHLORIDE ADMIXTURED L-ASPARAGINE MONOHYDRATE BY SLOW EVAPORATION TECHNIQUE

***Vela, T.**

Department of Physics, The M.D.T Hindu College, Tirunelveli-627010, India

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ABSTRACT

The title compound LAM prepared by using AR-grade L-asparagine and NaCl. It is dissolved in de-ionized water to get NaOH and HCl and these two are used as solvents. Solubility of LAM can be determined by gravimetric method. Using slow evaporation technique (SET), the grown crystal can be obtained in 20 days. The crystallanity of the crystal can be confirmed by X-ray diffraction. The crystals, by X-ray (EDAX) confirm the composition of elements in the crystal. The structure can be determined from Single X-ray diffraction. It shows that it belongs to orthorhombic system with space group $P2_12_12_1$. The various functional group associated with the crystal can be obtained from FTIR study. The NLO property can be confirmed by SHG test. It shows that, the grown crystal is 0.38 times that of KDP. The optional property of the grown crystal can obtained from UV-Visible transmittance study. The hardness of the grown crystal can be obtained from Vickers micro hardness test. The dielectric property and ac conductivity can be obtained from dielectric studies. From this activation energy can be obtained. An elementary analysis is carried out for the grown crystal by employing energy dispersive analysis.

INTRODUCTION

Crystals have special optical and electrical properties, in many cases, improved properties over randomly arranged materials. Many organic and inorganic materials are highly polarizable and are good candidates for Non Linear Optical (NLO) study. However, the net polarization of a material depends on its symmetry properties, with respect to the orientation of the impinging fields. Thus materials for second order NLO application must be orientationally non-centrosymmetric to be functional. NLO materials will be the key elements for future photonic technologies based on the fact that photons are capable of processing information with the speed of light. Second order NLO materials are used in optical switching (modulation), frequency conversion (SHG, wave mixing), and electro-optic applications, especially in EO modulators. All these applications are really on the manifestation of the molecular hyper polarizability of the material. The NLO property of the crystal finds in significant role device applications, which leads to the search for new NLO materials. As a result the research is concentrated primarily on organic compounds owing to their large nonlinearity. Jun Shen *et al.* (2003) have grown single crystals of L-tartaric acid-nicotinamide and D-tartaric acid-nicotinamide by the temperature lowering method from aqueous solution. Single crystal of 3-methyl 4-nitropyridine 1-oxide (POM) was grown by Boomadevi *et al.* (2004). Manivannan and Dhanushkodi (2007) have grown 3-((1E)-thylethanimidoyl)-4 hydroxy-6-methyl-2H-pyran 2-one, by slow evaporation technique and found that the SHG efficiency is close to that of urea. L-arginine acetate (LAA) is an organic nonlinear optical material which has a wide optical transmission window between 220 and 1500 nm. Its laser damage threshold and SHG efficiency are comparable with that of KDP. It was grown by Tanusri Pal *et al.* Vickers microhardness measurement was also done for different crystallographic planes of LAA by Tanusri Pal and Tanusree Kar (2004). An organic electro-optic and nonlinear optical (NLO) crystal, L-alaninium oxalate (LAIO), was grown and its physicochemical properties was studied by Dhanuskodi and Vasantha (2004) then by Vimalan *et al.* (2007). L-asparagine is an organic amino acids group because it contains one amino (NH_3^+) and two carboxylic acid groups (COO^-). It is non-essential or also dispensable aminoacids because this aminoacids which can be synthesized by the body and therefore need not be supplied through the diet. In order to retain the merits and overcome the shortcomings of organic materials, some new classes of NLO crystals such as metal organic or semiorganic complex crystals have been developed. The relatively strong metal ligand bond permits the complex crystals to combine the advantages of inorganic crystals, such as good stability, with the advantages of organic crystals, such as high nonlinearity and molecular engineering features.

The search for novel crystals with nonlinear optical properties is still a challenge for scientists. To fulfill the “molecular engineering” of nonlinear optical crystals, two theoretical models suitable respectively for the studies of the absorption

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****Corresponding author: Vela, T.***
Department of Physics, The M.D.T Hindu College, Tirunelveli-627010, India

edge and birefringence of a nonlinear optical crystal have been set up by Kuchen Wu *et al.* (2007). The family of the various borate crystals plays a very important role in the field of nonlinear optics (1975).

The overwhelming success of molecular engineering in controlling non-linear optical (NLO) properties has attracted the attention of researchers to search for a variety of new types of NLO materials (Marder *et al.*, 1989; Lakshmana Perumal *et al.*, 2002). However, the implementation of single crystals of organic materials in practical device applications has been impeded by their inadequate transparency, poor optical quality and low LASER threshold. Inorganic crystals have excellent mechanical and thermal properties, but they possess relatively modest non-linearity because of the lack of π electron delocalization. Hence recent search is concentrated on organometallic materials due to their large nonlinearity, high resistance to LASER induced damage, low angular sensitivity and good mechanical hardness (Xing *et al.*, 1987; Veslo 1990). Now-a-day the organic and inorganic materials are being replaced by semiorganic materials because they share the properties of both organic and inorganic materials. Also the semiorganic materials show large nonlinearity, low angular sensitivity and good mechanical hardness. In the case of metal-organic coordination complexes the organic ligand is usually more dominant in the nonlinear optical (NLO) and dielectric effects. The semiorganic nonlinear optical thiosemicarbazide cadmium chloride monohydrate (TCCM) single crystals are grown and its optical and birefringence studies are done by Manivannan *et al.* (2007).

In this context it is motivated to study about a semi metallo organic compound. Amino acids play a vital role in the field of science and technology. Among organic crystals for non linear optics (NLO) applications, α-aminoacids display specific features of interest, such as molecular chirality, which secures acentric crystallographic structures; absence of strongly conjugated bonds, leading to wide transparency ranges in the UV-Visible spectral regions; zwitterionic nature of the molecule, which favours crystal hardness. Further to that amino acids can be used a chiral auxiliary for nitro-aromatics and other donor – acceptor molecules with large hyper polarizabilities. An interesting class of materials receiving wider attention in recent past includes the analogs of amino acids like L-arginine, L-histidine, L-alanine, etc. Among the amino acids L-arginine and L-histidine have been exploited for the formation of salts with different organic/inorganic acids. As a result, good semiorganic NLO materials such as L-arginine phosphate monohydrate, l-histidine tetrafluroborate (LHFB) have been developed and are found to be suitable in number of NLO applications. However a very few complexes incorporating L-alanine have been crystallized and studied (Razetti *et al.*, 2002; Dhanuskodi and Ramajothi 2004; Dhanuskodi and Vasantha 2004; Vasantha and Dhanuskodi 2004; Justin Raj and Jerome Das 2007; Neelam Singh *et al.*, 2008; Jai Kumar *et al.*, 2009; Jai Kumar *et al.*, 2010). The metallo organic compound L-alanine cadmium chloride (LACC) was first synthesized by Kathleen *et al.* (1993) and later its structural and optical properties were studied by Dhanuskodi *et al.* (2007) and then Justin Raj *et al.* (2008) have grown bulk crystal of LACC by S.R. method. In the present work the single crystals of LAM crystals were grown by a simple slow evaporation technique by using NaOH and Hcl as solvents and they are characterized by different characterization techniques such XRD, FTIR , UV, Microhardness etc.

Experimental procedure

Solution solubility

A solution is a homogeneous mixture of a solute in a solvent. Solute is the component which is present in a smaller quantity and that one which gets dissolved in the solution. For a solute there may be different solvents. Solubility of the material in a solvent decides the amount of the material which is available for growth and hence defines the total size limit. Solvents commonly used are water, ethanol, methanol, acetone, carbon tetrachloride, hexane, sodium hydroxide, hydrogen chloride etc. Solubility gradient is another important parameter which dictates the growth procedure. If the solubility gradient is small, slow evaporation of the solvent is the other option for crystal growth to maintain supersaturation in the solution. In the present work NaCl is dissolved in deionised water. It gives NaOH and HCl and these are used as solvents. The solubility curve of the grown crystal is shown in Figure 1.

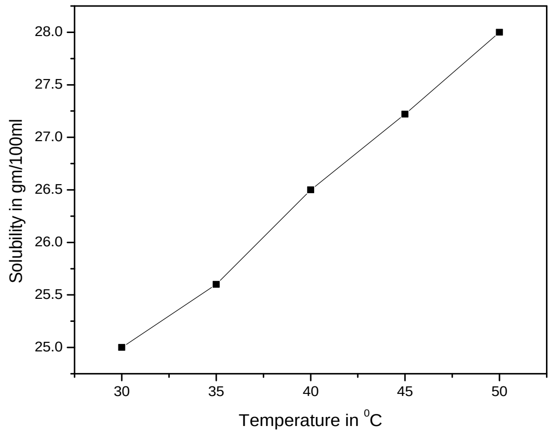

Fig. 1.

Synthesis and growth

Analytical Reagent (AR) grade L-asparagine, NaCl and distilled water are used for synthesis and growth. By taking these two as in the ratio 2:1 and they were very well dissolved in deionized water and it was thoroughly mixed using a magnetic stirrer for about 2hrs.

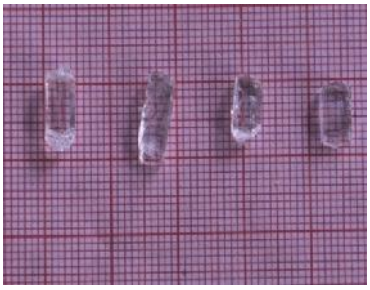

Fig. 2. Photograph of as-grown crystal

Single crystal of LAM was grown by solution growth employing slow evaporation technique at room temperature

(Sunil Verma *et al.,* 2000; Sonal Gupta and Rangith, Pradhan 2002; Arunmozhi *et al.,* 2004; Chang *et al.,* 1990; Vasantha and Dhanuskodi 2002; Ramabadran *et al.,* 1992; Venkataramanan *et al.,* 1994). The grown crystal is shown in Fig. 2.

Characterization Techniques

In the present study, LAM crystal using disolvents were subjected to various characterizations such as X-Ray diffraction (XRD) analysis, Fourier Transform Infra Red (FTIR) spectroscopy, Energy Dispersive Analysis by X-ray (EDAX), Thermo Gravimetric /Differential Thermal (TG/DT) analysis, Vicker's microhardness test, UV-Visible optical analysis, Second Harmonic Generation (SHG) measurements and electrical studies.

Single crystal X-ray diffraction analysis

Single crystal X-ray diffraction is an analytical technique in which X-rays (wave length range from 0.1 to 10 Å) are employed to determine the actual arrangement of atoms within a crystalline specimen. Single crystal X-ray diffraction (XRD) is a non-destructive tool to analyze crystal compounds, which can be grown as single crystals. The molecular structure, atomic coordinates, bond length, bond angles, molecular orientation and packing of molecules in single crystals can be determined by X-ray crystallography. With the set of X-ray diffraction data collected, unit cell parameters, space group, molecular structure, etc of the crystalline solids and Miller indexing of the different faces of the crystal are possible. Unit cell parameter is simply the dimension of the basic molecules with which the crystal is built. Space group tells us the symmetry with which the molecules are arranged within the unit cell. All the geometrical features of molecules (bond distance, bond angles, torsion angles between bonds, dihedral angles between planes etc.) may be obtained from coordinates. In the present study, the single crystal X-ray diffraction analysis was performed using an Enraf Nonius CAD4 single crystal X-ray diffractometer.

Powder X-ray diffraction analysis

The powder diffraction of a substance is characteristic of the substance to be identified. The peaks of the X-ray diffraction pattern can be compared with the standard available data for the confirmation of the structure. The powder X-ray diffraction method was devised independently by Debye and Scherer. In the present study the powder filled sample holder was kept on the goniometer cell of XRD system (Philips, model: *X'pert pro*) employing *X'celerator* and a monochromator on diffracted beam side. Scans were made in $2\theta^0$ usually at 0.01^0/step. Most of the scans were done by applying 40kV tube potential difference and 30 mA current. CuKα1 radiation (λ = 1.540566 Å) was used for all measurements. Powder X-ray diffraction is useful for confirming the identity of a solid material and determining crystallinity and phase purity. Many books give details of principles and methods involved in the determination of crystal and molecular structures of inorganic and organic substances (Klug and Alexander 1954; Stout and Jensen 1968; Wolfson 1970; Buerger 1958; Chan 1961; Griffths and De Hoseth 1986).

Fourier Transform Infrared (FTIR) spectroscopic technique

Infrared spectroscopy is the study of the interaction of infrared light with matter. The fundamental measurement obtained in infrared spectroscopy is an infrared spectrum, which is a plot of measured intensity versus wavelength (or wave number) of light. An instrument used to obtain an infrared spectrum is called an infrared spectrometer. There are several kinds of spectrometers in the world used to obtain infrared spectra. The most prevalent type of spectrometer is called a Fourier Transform Infrared Spectrometer (FTIR). FTIR technique is most useful for identifying functional groups organic and inorganic compounds. It can be applied to the analysis of solids, liquids and gases. In the present work, the FTIR spectrum of the sample was recorded with a Fourier transform infrared spectrometer in the range of 400 -4000 cm^{-1}following KBr pellet technique.

Energy dispersive analysis by X-ray (EDAX)

X-rays are produced when materials are irradiated with a high energy electron beam. The wavelength and hence the energies of the X-rays are characteristic of the electron shell energies of the respective atoms and hence the spectrum of X-rays can be used to identify different elements and also possible to measure the amount of different elements present in the material. In energy dispersive spectrometer, the diffraction is not involved, the various wavelengths in which the radiation is emitted by the sample are separated by means of a silicon-lithium (Si-Li) detector and each signal is collected, amplified and corrected for absorption and other effects, to give both qualitative and quantitative analysis of the composition of the specimen as a whole or an area of interest (for elements of atomic number greater than 11). This technique is known as Energy Dispersive Analysis by X-ray EDAX or EDX).

Thermal Analysis

Thermal methods are based upon the measurement of the dynamic relationship between temperature and some property of a system such as mass, heat of reaction of volume. Of the various thermal methods, *Thermo Gravimetric Analysis* (TGA) and *Differential Thermal Analysis* (DTA) are most important (Wendlandt 1974). The TGA provides a quantitative measurement of any weight changes associated with thermally induced transitions. For example, TGA can record directly the loss in weight as a function of temperature or time (when operating under isothermal conditions) for transitions that involve dehydration or decomposition (Wunerlich 1990; Brown 1988). Thermo gravimetric curves are characteristic of a given compound or material due to the unique sequence of physical transitions and chemical reactions that occur over definite temperature ranges. The TGA curves gives information regarding the thermodynamics and kinetics of various chemical reactions, reaction mechanisms, intermediate and final products. In DTA, the difference in temperature between the sample and a thermally inert reference material is measured as a function of temperature (usually the sample temperature). Any transition that the sample undergoes results in liberation or absorption of energy by the sample with a corresponding deviation of its temperature from that of the reference. As the temperature of both is increased at a constant rate, the corresponding deviation of the sample temperature from that of reference (ΔT) versus the programmed temperature (T) is recorded and it explains whether the transition is endothermic or exothermic. The DTA studies along with TGA provide detailed information regarding the dehydration, decomposition and the phase transitions of a material during heating. In the present study the thermal characteristics of the grown crystals were studied using Perkin TG/DTA analyzer.

Micro hardness Measurements and Vickers hardness test

Hardness is one of the important properties which crystals should possess for device applications. Hardness is a measure of resistance against lattice destruction or the resistance offered to permanent deformation or damage. Measurement of hardness is a non-destructive testing method to determine the mechanical behavior of the materials (Shaw 1973). For hard and brittle materials, the hardness test has proved to be a valuable technique in the general study of plastic deformation. Meyer established a relationship between indentation hardness and work hardening capacity of a material (Westbrook and Conrad 1971). Again hardness test provides useful information on the strength and deformation characteristics of material (Mott 1956). The Vickers hardness number is calculated using the relation $H_v = 1.8544P/d^2$ kg-mm^{-2} where P is the applied load in kg and d is the diagonal length of the indentation mark in mm. In the present study the microhardness measurements were made using a Leitz microhardness tester fitted with a diamond pyramidal indentor.

UV-Visible Spectrophotometry

UV-Vis-NIR spectral measurements are done in the case of grown crystals, so as to find how far the crystals can be used in these spectral regions. If the sample transmits the incident light in the entire UV-Vis-NIR regions with out any significant absorption then that sample would be a good candidate for optical applications in those regions. An UV-Visible spectrophotometer allows light of a given frequency to pass through a sample and detects the amount of transmitted light. The instrument compares the intensity of the transmitted light with that of the incident light. The source of radiation in the UV-Visible spectrophotometer is tungsten, hydrogen or deuterium lamp. A source of radiation may be provided with each spectral region having its own requirements. In the present study the UV-Visible transmittance of the grown crystal was recorded using a Varian Cary 5E UV-Vis-NIR spectrophotometer in the range of 200-1200nm to find the transmission range and hence their suitability for optical applications.

Nonlinear Optical Phenomenon-Kurtz Powder SHG Method

Nonlinear Optics (NLO) is the study of the interaction of intense electromagnetic field with materials to produce modified fields that are different from the input field in phase, frequency or amplitude (Firdous Anwar 1988). An optical process in which an input optical wave is converted into an output wave or twice the input frequency is called Second harmonic generation (SHG) (Chemla and Zys 1987). This process occurs within a nonlinear medium, usually a crystal. Such frequency doubling process is commonly used to produce green light (532 nm) from, for example, a Nd: YAG (yttrium-aluminium-garnet) laser operating at 1064 nm. The light propagated through a crystalline solid, which lacks a center of symmetry (noncentrosymmetric), generates light at second and higher harmonics of the applied frequency. Nonlinear optics is completely, a new effect in which light of one wavelength is transformed to light of another wavelength. The creation of light of new wavelength can be best understood, as we think about the electrons in nonlinear crystal. Second order NLO materials are used in optical switching (modulation, frequency conversion, SHG wave mixing), and electro-optic applications. Kurtz and Perry (Kurtz and Perry 1968) proposed a powder SHG method for comprehensive analysis of the second order nonlinearity. Employing this technique, Kurtz surveyed a very large number of compounds. In this method the nonlinear optical property of the grown single crystal is tested by passing the output of Nd:YAG Quanta ray laser through the crystalline powder sample.

Dielectric and Ac conductivity measurements using LCR meter

Dielectric constant is a number relating the ability of a material to carry alternating current. The capacitance created by the presence of the material is directly related to the dielectric constant of the material. Knowing the dielectric constant of a material is needed to properly design and apply instruments such as level controls using radar, RF admittance, or capacitance technologies. In order to carry out dielectric measurements, the grown crystals were polished in proper size and for good electrical contact opposite faces of the sample crystals were coated with good quality graphite. The samples were annealed in the holder assembly at 383 K before making observation. The dimensions of the crystals were measured using a travelling microscope and the area of contact (1xb) of the sample with the electrodes was calculated. The capacitance (C_{crys}) and dielectric loss factor (tan δ) are measured to an accuracy of $\underline{+}2$ % using Agilent 4284A Precision LCR meter with five different frequencies, viz.100 Hz, 1 kHz, 10 kHz and 1 MHz from temperature 303 to 383 K along the b-axis of the crystal in a way similar to that followed by Goma *et al.* (2006) and Manonmani *et al.* (2007). Temperature was controlled to an accuracy of $\underline{+}1^0$C. The samples were prepared and annealed in a way similar to that followed for the resistance measurement. The AC conductivity (σ_{ac}) was calculated using the relation,

$\sigma_{ac} = \varepsilon_o \, \varepsilon_r \omega \tan\delta$,

Where ε_o is the permittivity of free space (8.85 x 10^{-12} C^2 N^{-1} m^{-2}) and ω is the angular frequency.

AC Activation energy

AC activation energy of a substance is the minimum energy required for the atoms or molecules in the compound to activate while an AC voltage is applied. The dependence of

AC conductivity on temperature is usually obey the well known relation (El-Desky *et al.,* 2001)

$\sigma_{ac} = \sigma \exp(-E_{ac}/KT)$

Where K is the Boltzmann's constant, T is the absolute temperature, σ is the constant depending on the material and E_{ac} is the AC activation energy.

The above equation can be written as

$\ln \sigma_{ac} = \ln \sigma - E_{ac}/KT$

This is equation for a straight line. A plot of $\ln \sigma_{ac}$ versus (1/T) gives E_{ac}/KT as the slope and $\ln \sigma$ as the y-intercept. It is customary to plot $\underline{\ln \sigma_{dc}}$ versus (1000/T), from the slope of which the activation energy (E_{ac}) can be calculated.

Actually this is the energy required for the process such as direct interchange between the two atoms, migration of an interstitial atom subsequent to formation of a Frenkel defect, atomic displacement into a neighboring vacancy subsequent to formation of a Schottky defect, diffusion of pairs of vacancies by means of atomic movements in to either of vacancies, that is the sum of energies of defect formation and subsequent migration is called the activation energy.

RESULTS AND DISCUSSION

Single XRD

The obtained unit cell dimensions of the grown crystal using disolvents is shown in the Table1.

Table 1. Single crystal XRD data for the grown crystals

Crystal Parameters	LSLA crystal
a (Å)	5.571(5)
b (Å)	9.784(2)
c (Å)	11.758(4)
α	90°
β	90°
γ	90°
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Volume($Å^3$)	640.9(3)
Z	4

Powder XRD diffraction measurements

X-ray powder diffractometry is the most powerful technique for structural analysis, capable of providing information about structure of a material at the atomic level. X-ray diffraction data gives the angle of scattering (2θ) and the corresponding intensities of diffracted beam for each reflection. An advance X-ray diffractometer (PANalytical-MPD) was used to take the diffraction patterns of the crystals with Cuk_α radiation of wavelength λ = 1.54056 Å. The samples were scanned over the required range for 2θ ($0\text{-}70^0$) at a scan speed of 30^0/s. The analysis of the spectra confirmed the crystalline nature of the samples. X-ray powder diffraction data of the crystals are presented in the Table 2.

Indexing the Data

Indexing of a powder pattern consists of the assignment of the three numbers h,k,l (Miller indices) to each reflection. All the reflections of powder XRD patterns of the grown crystals in powder form were indexed using the software. The indexed X-ray powder diffraction patterns of the grown crystals in powder form are given in the Figure 3.

Table 2. X-ray powder diffraction data of the crystals

Peak No	2θ in degree	d (Å)	hkl
1	11.820	7.480	001
2	17.631	5.026	101
3	18.159	4.881	020
4	19.628	4.519	021
5	21.998	4.037	102
6	23.702	3.750	112
7	25.342	3.511	121
8	27.436	3.248	103
9	28.309	3.149	031
10	28.647	3.113	122
11	31.804	2.811	130
12	33.049	2.708	201
13	35.267	2.542	132
14	37.505	2.396	041
15	39.224	2.294	124
16	42.641	2.118	025
17	43.148	2.094	142
18	43.857	2.062	223
19	45.519	1.991	232
20	47.550	1.910	035
21	53.147	1.721	234
22	53.930	1.698	045
23	55.040	1.667	322
24	66.306	1.408	028

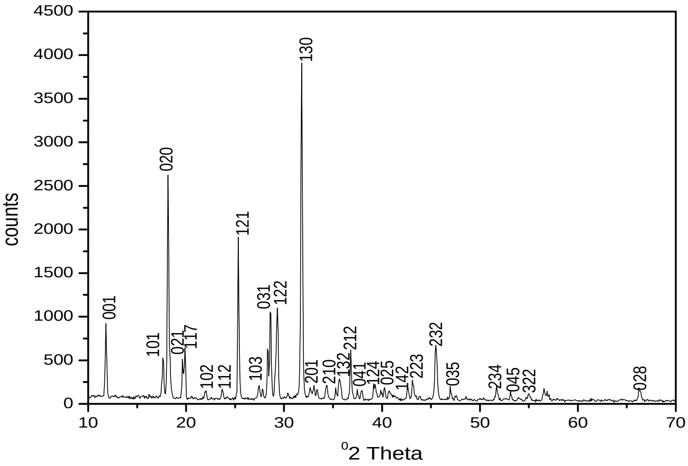

Fig.3. Powder XRD of the grown crystal

FTIR Studies

The infrared spectroscopy is an important tool in the investigation of the functional groups of crystals. Infrared radiation promotes transitions in a molecule between rotational and vibrational energy levels of the ground electronic energy states. It gives information about certain groups of atoms or functional groups present in the material. The FTIR spectra of the grown crystalline samples were recorded using KBr pellet method by SHIMADZU (FTIR-8400S) spectrometer in the spectral range of 400-4500 cm^{-1}. The FTIR spectra of the grown crystals are displayed in the Fig 2 and FTIR bands/peaks and their assignments are given in the Table 3.

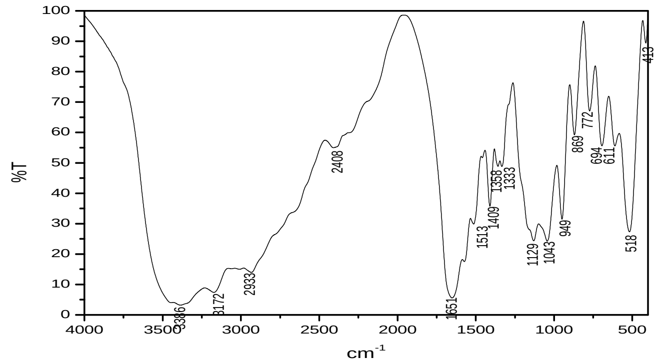

Fig. 2. FTIR study of the grown crystal

Table 3. Functional assignments of the grown crystal

Bands/Peaks (cm^{-1})	Band assignments
3386	NH asymmetry stretching vibration
3172	NH_2 Symmetry stretching
2933	CH_2 asymmetry stretching
2403	Overtones and combinations
1661	NH^{3+}bending degenerate
1513	Stretching N-C-N
1409	Coo$^-$ symmetry Stretching
1388	CH_3 Symmetry bending
1333	CH_3 Symmetry bending
1129	Phenolic O
1043	C-N stretching
949	C-N Symmetry stretching
869	C- C-N Symmetry stretching
772	o-c-o deformation
694	Coo$^-$Scissoring
611	C-N and C=O bending
518	Coo$^-$ rock

Energy Dispersive Analysis by X-Ray

An elemental analysis is carried out for the grown crystal by employing *Energy Dispersive Analysis by X-ray* (EDAX) in order to confirm the composition of elements in the grown crystal. Figure 3 shows the EDAX spectrum of the grown crystal. Again table 4 gives the composition of all the elements and the percentage of atoms present in the grown crystal.

Table 4. Elemental composition of the grown crystal

Element	*Net Counts*	*Weight %*	*Atom %*
C	16490	24.30	29.16
N	13607	30.31	31.18
O	36868	41.58	37.45
Na	10609	2.51	1.57
Cl	4933	1.30	0.64

Ultraviolet-Visible Spectral Studies

The absorption of radiation causes the molecule or atom to be in an excited state. Frequency of absorbed radiation provides a means of characterizing the constituents of a sample of matter. For this purpose transmission is plotted against wavelength or frequency. The plots of this type are known as transmission spectra. Ultraviolet region extends from 1000-4000 Ǻ and visible light ranges from 4000-7000 Ǻ. For single crystals mainly used in optical applications, the optical transmittance range and the transparency cut-off are important. A Varian Cary 5E UV-Vis-NIR spectrophotometer was used for spectra transmission studies.

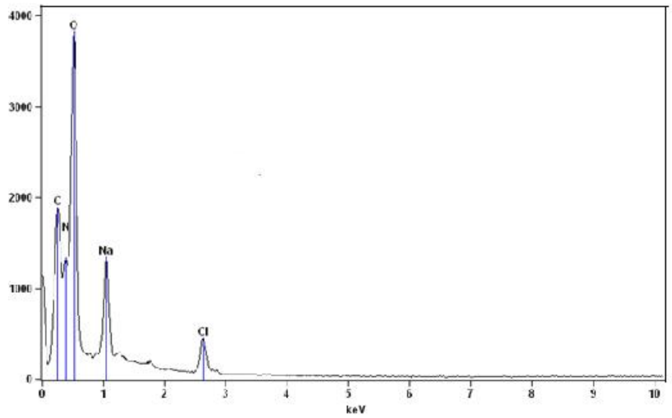

Fig. 3. The EDAX plot of the grown crystal

The recorded transmittance spectra of grown crystals are shown in Figure 4.

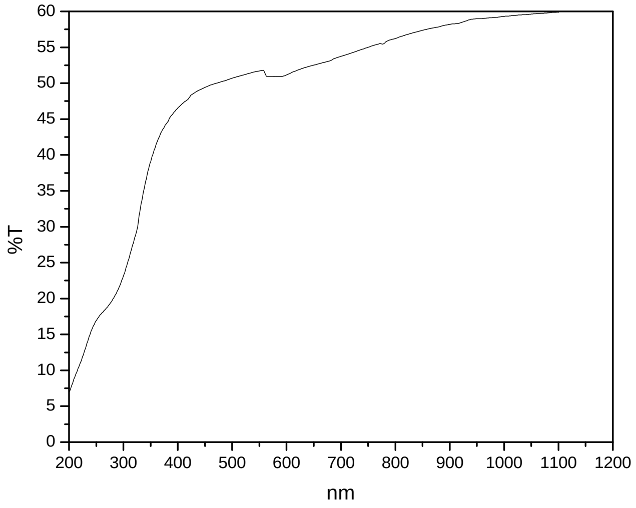

Fig. 4. Transmittance spectra of the grown crystal

It is noticed that the cut-off wavelength for the grown crystal is 250nm. The forbidden band gap for the grown crystals of this work was calculated using the relation E=hc/λ where h is the Plank's constant, c is the velocity of light and λ is the wavelength of light. The obtained value for the forbidden band gap for all crystals is 4.963 eV. This indicates that all the grown crystals are insulators. Since the cut-off wavelength occurs in UV region, the grown crystals are useful to be NLO materials. The Second Harmonic Generation (SHG) test has been carried out to confirm NLO property.

Microhardness study

Microhardness measurements were done using a Vicker's micro hardness indenter (Leitz weitzier hardness tester). In the present work, indentations are made on (100) for five loads 15,20,25,40 and 50 g and indentation time given is 10 s. For each load, several indentations are made and the average diagonal length (d) is used to calculate the microhardness number. Vicker's hardness number H_v is calculated using the relation

$H_v = 1.8554\ P/d^2\ Kg\ mm^{-2}$

Where P is the load applied in Kg and d is the diagonal length of the indented impression in mm.

A plot between the hardness values and the corresponding loads for the grown crystal is drawn and they are provided in the Figure 5.

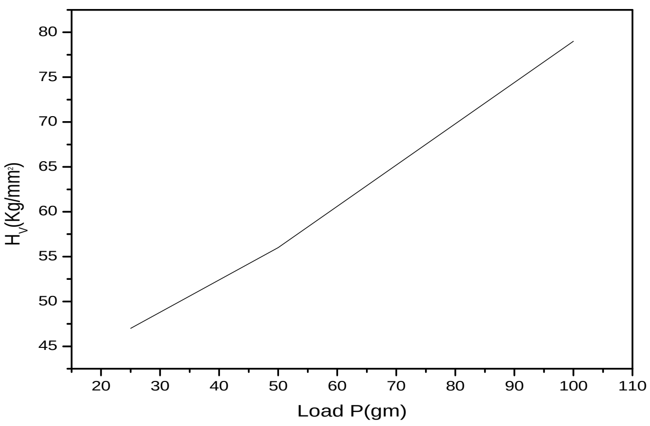

Fig. 5.Variation of hardness number with applied load for the grown crystal

From the results, it is observed that hardness number increases as the load increases for sample of this work. The relation between the load and size of indentation is given by Meyer's law as $P=a\ d^n$ where P is load in Kg, d is the diameter of recovered indentation in mm, a is a constant and n is the work hardening coefficient. The plot log p against log d is a straight line, which is shown in Figure 6.

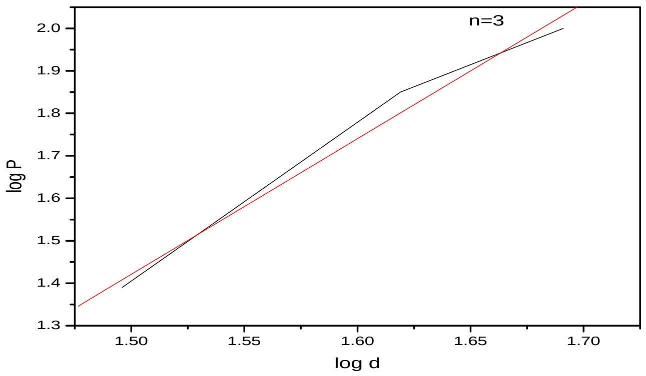

Fig. 6. Plot of log P versus log d for the grown crystal

The slope of the straight lines of the figure 6 gives the work hardening coefficient n = 3.451. Careful observations of Onitsch (1947), Hanneman (1941) and Kishan Rao *et al.* (2002) on various materials have pointed out that n lies between 1 and 1.6 for hard materials and it is more than 1.6 for soft materials. According to Onitsch, if n is greater than 1.6, the microhardness number increases with increase in load. Since the obtained values of n for the grown crystal is more than 1.6, the grown crystals of this work belong to the category of soft materials.

Thermal analysis

The Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) of the sample crystals were carried out. The analyses were carried out simultaneously in air at a heating rate of 20^0C/minute for a temperature range of 30-1100^0C. TGA-DTA curves of the grown crystals are displayed in figure 7. DTA curve in Figure 7 shows that the grown crystal melts at 102^0Cand it undergoes endothermic transitions (peaks) at 250^0C, 500^0C and 850^0c. The TGA curve shows that there is a weight loss in the temperature range 102^0C due to the liberation of volatile substances probably sulphur oxide in the compound.

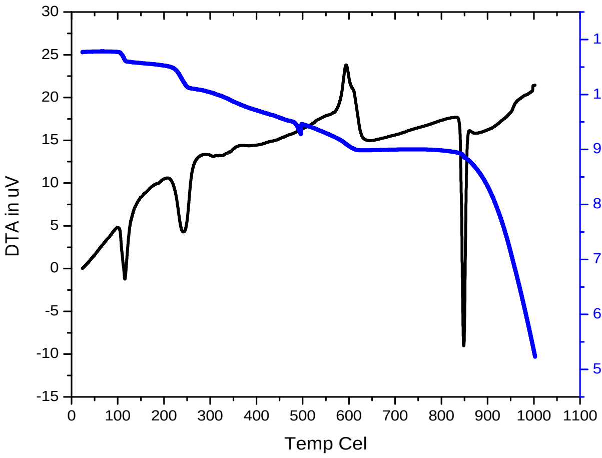

Fig.7.TG/DTA curves for the grown crystal

Non Linear Optical

The Powder SHG measurement for the grown crystal was performed using the Kurtz and Perry powder technique. The finely powdered sample was densely packed between two transparent glass slides. A fundamental laser beam of 1064 nm wavelength (8 ns pulse width with 10 Hz pulse rate) from an Nd-YAG LASER was made to fall normally on the sample cell. The power of the incident beam was measured using a power meter. The input LASER energy incident on the capillary tube was 4.3 mJ/5.3 mJ per pulse, an energy level optimized not to cause any chemical decomposition in the sample. The KDP crystal was used as the reference material in the SHG measurement. The NLO property of the crystal was confirmed by the Kurtz and Perry powder technique. The transmitted fundamental wave was passed over a monochromator which separates 532 nm (second harmonic signal) from 1064 nm and absorbed by a $CuSO_4$ solution which removes the 1064nm light. The green light was detected by a photomultiplier tube and displayed on a storage oscilloscope. The powder SHG efficiency of the crystal is 0.35 times that of KDP.

Measurement of dielectric constant and dielectric loss

The dielectric parameters such as dielectric constant and dielectric loss of crystalline samples were measured using a two-probe arrangement and an LCR meter. Frequency dependence of dielectric constant (ε_r) and dielectric loss (tan δ)

of the pure grown crystals at various temperatures are displayed in the Figure 8 and Figure 9. The dielectric measurements were taken for all the samples of this work with the electric field along the ferroelectric axis (b-axis). Dielectric parameters are observed to be decreasing with increase in frequency. Beyond the frequency of 10^4 Hz, the dielectric parameters are found to be practically independent of frequency.

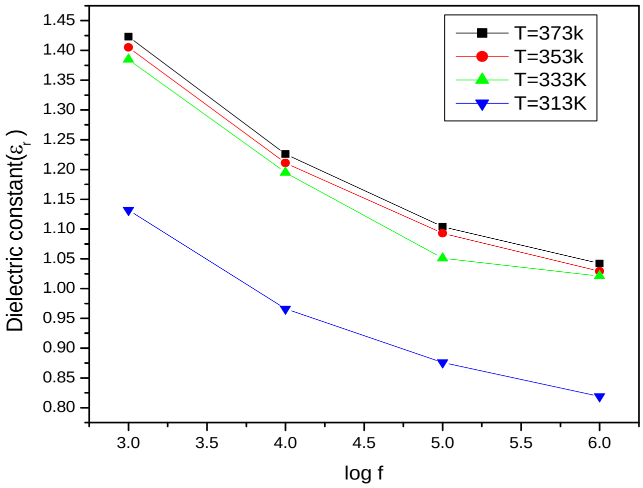

Fig. 8. Variation of Dielectric constant with frequency

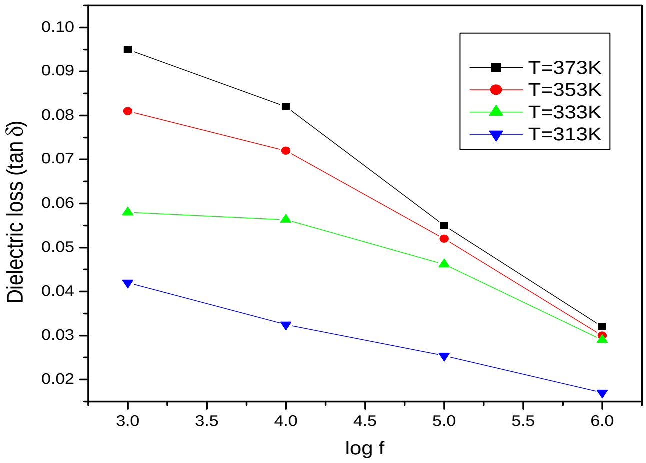

Fig. 9. Variation of Dielectric loss with frequency

AC conductivity Study

The ac conductivity measurements were carried out using an LCR meter in the frequency range 1 KHz-1 MHz. The sample was heated in the temperature range 30° to 100°C.The ac conductivity was calculated using the formula, $\sigma_{ac}= \omega\varepsilon_o \varepsilon_r \tan\delta$ at different temperature. Figure 10 shows the plot of ac conductivity versus 1000/T. It is evident from the graph that the conductivity increases with temperature. The Arrhenius Plot of $\ln\sigma_{ac}$ versus 1000/T is shown in Figure 11. The activation energy for ionic migration was estimated from the graph. The line of best fit for the plot of $\ln\sigma_{ac}$ versus 1000/T obeys Arrhenius relationship $\sigma_{ac}= \sigma_o \exp(-E_{ac}/KT)$ where σ_o is the pre-exponent factor, E_{ac} is the activation energy for the conduction process and K is the Boltzmann constant. Therefore the sample exhibits Arrhenius type conductivity behaviour in the temperature range of investigation. The activation energy of the grown crystal for the conduction process calculated from Fig.10 and it is found to be 0.7452eV.

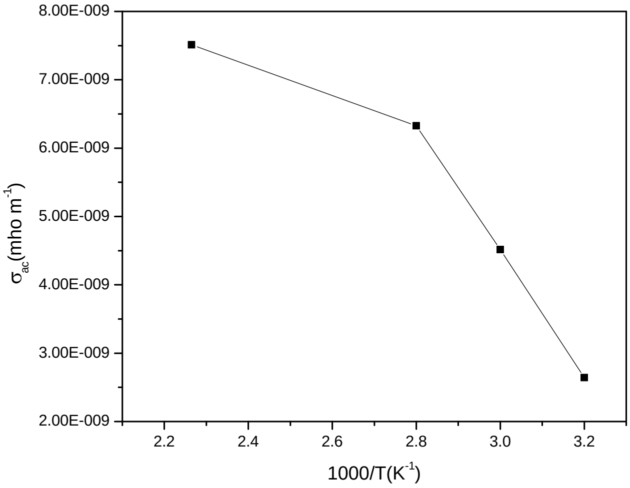

Fig. 10.Variation of ac conductivity with 1000/T

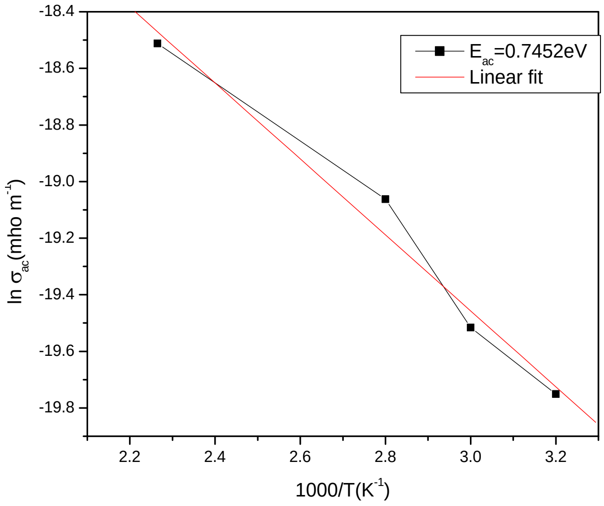

Fig. 11. Plot of $\ln\sigma_{ac}$ versus 1000/T

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