GROWTH AND CHARACTERIZATION OF NON LINEAR OPTICAL UREA AMMONIUM CHLORIDE SINGLE CRYSTALS

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I. ABSTRACT

Single crystals of Ammonium chloride doped with Urea an organic material: have been grown by slow evaporation technique at room temperature.The crystalline nature of grown crystal was confirmed by micro hardness Analysis. The functional group of the grown crystals was found by FTIR analysis. The spectral bands have been compared with similar thiourea complexes using the FTIR spectrum in the range 400-4000 cm-1. The UV- Vis study was performed to know the optical behavior of the grown crystals.

KEY WORDS: Urea, UV-Analysis, Micro hardness, FTIR.

II. INTODUCTION

The study of growth and characterization of a single crystal is receiving increasing importance due to their wide applications in solid-state technology and the fascinating area of lasers. The laser technology forms the backbone of modern scientific developments well-characterized single crystals are necessary fundamental research as well for device fabrication. The growth of perfect and dislocation free single crystals [1]. With the advent of high power lasers, there is an interest in the nonlinear optical single crystals which play important role in electro-optic modulation, optical memories, signal processing, signal amplification etc. [2].

The phenomenon of crystal growth is widely observed in nature and it is found to occur in several ways, depending upon the system involved. Some commonly observed growths in nature are the formation of ice, sapphire,andrubyorotherpreciousstones,quartzetc.Thewordcrystalis aGreekword whichmeansiceandin olden days this name was given to all those stones which were as clear as ice. It appears that the formation of natural crystals in nature and their observations must have provided the first clue for the growth of crystals in laboratories. In due course of time, a better understanding of the growth process has led to the development of several techniques for the growth of singlecrystals.

The process of crystal growth essentially involves the change of phase where the molecules of the material undergoing the phase change are gradually, uniformly and continuously losing their random character are achievingacrystallinesolidcharacterwhichhaslongrangeorder[3]Theformationofcrystalgeneraltakesplace two steps namely nucleation and bulk growth. The process which results in the formation of tiny solid phase the midstofrandomnessistermedasnucleationandthesolidphasethusappearedasnucleus.Thesubsequentgrowth of nucleus into bulk crystal is classified as the bulk growth. The phase transformation resulting in nucleation or the bulk growth is always accompanied by a change in free energy of the system. The overall change in the free energy in the case of nucleation is much larger than that associated with bulkgrowth.

Theshapesof crystalsdependonboththeinternalsymmetryofthematerialandontherelativegrowthrateof the faces. In general, the faces of the crystal that grow most rapidly are those to which the crystallizing particles are tightly bound. These rapidly growing faces are usually the smaller and not well-developed faces. Thus the larger faces are usually associated with directions in the crystal where there are only weak intermolecular interactions [4].

III. EXPERIMENTAL TECHNIQUE

SLOW EVAPORATIONMETHOD

This method is similar to the slow cooling method. The temperature is fixed constant and the provision is made for the evaporation of the solvent. Then, the growth rate is controlled by controlling the evaporation rate. In almost all cases, the vapor pressure of the solvent above the solution is higher than the vapor pressure of the solute. Therefore the solvent evaporates more rapidly and the solution becomes super saturated [27]. With non- toxic solvents like water, it is permissible to allow evaporation into the atmosphere. Typical growth conditions involve temperature stabilization to about 0.01c and rates of evaporation of a few 3mm/hr. This method can be used with materials, which have very small temperature coefficient of stability

FOURIER TRANSFORM INFRARED SPECTROSCOPY(FT-IR)

FT-IR is an analytical technique used to identify organic, polymeric and inorganic materials. The FT-IR analysismethodusesininfraredlighttoscantestsamplesandobservechemicalproperties.Itisatechniqueused to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high-spectral resolution data over a wide spectral range. This confers a significant advantageoveradispersivespectrometer,whichmeasuresintensityoveranarrowrangeofwavelengthsatatime.

FTIR is a method of obtaining infrared spectra by first collecting an interferogram of a sample signal using an interferometer, and then performing a Fourier transform on the interferogram to obtain the spectrum. An FTIR spectrometer collects and digitalizes the interferogram, performs the FT function and display the spectrum. The actual calculation of the Fourier transform of such systems is done by means of high speed computers[38]

UV-VISIBLE SPECTROSCOPY

UVistypeof absorptionspectroscopyinwhichlightofultra-violetregion(200400nm)isabsorbedbythe molecule. Absorption of the ultra-violet radiations result in the excitation of the electrons from the ground state to higher energy state. The energy of ultra-violet radiation that are absorbed is equal to the energy difference between the ground state and higher energy states. ($\Delta E=hf$) Generally, the most favoured transition is from the highest occupied molecular orbital to the unoccupied molecular orbital. For most of the molecules, the lowest energy occupied molecular orbitals are s orbital, which correspond to σ bonds. The p orbitals are at somewhat higher energy levels, the orbitals (nonbonding orbitals) with unshared paired of electrons lie at higher energy levels. The unoccupied or antibonding orbitals (π^* & σ^*) are the highest energy occupied orbitals. In all the compounds (other than alkanes), the electrons undergo various transition. Some of the important transitionswith increasing energies are: nonbonding to π^*, nonbonding to σ^*, π to π^*, σ toπ^*

MICROHARDNESS

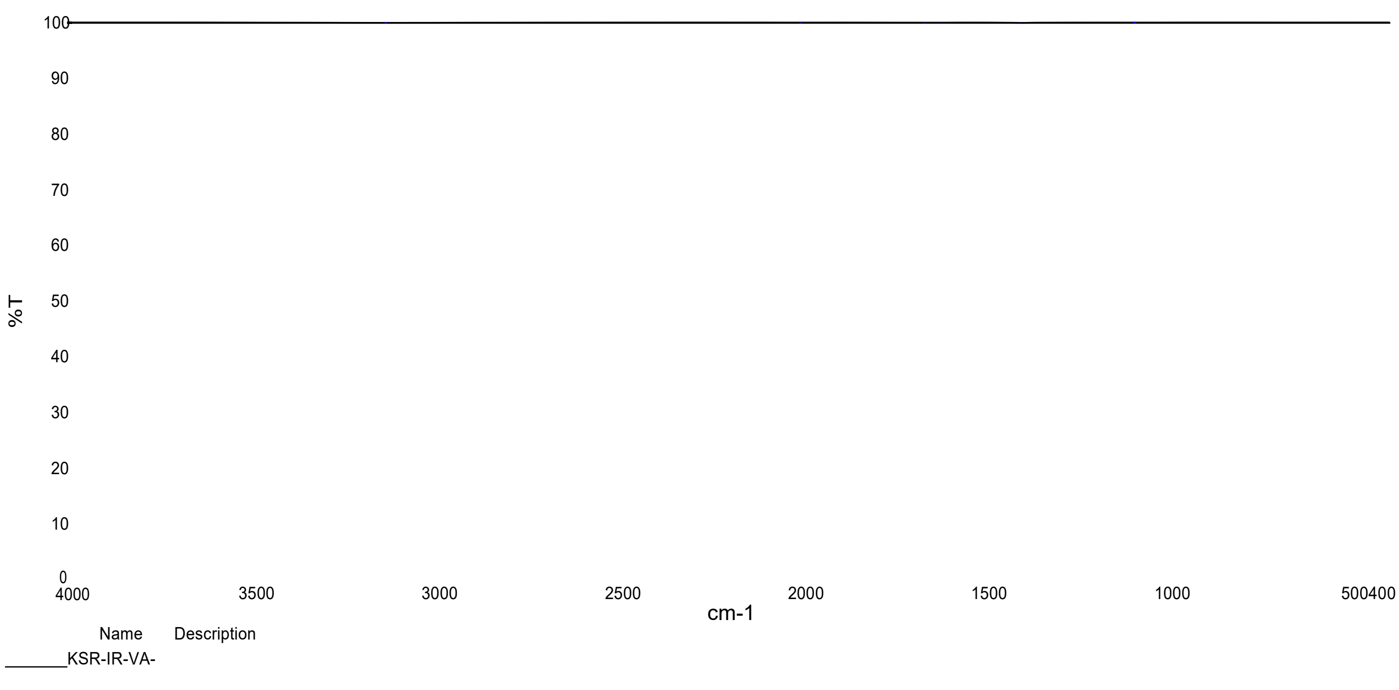
Micro hardness testing is a method of determining a material's hardness are resistance to penetration when test samples are very small or thin, or when small region in a composite sample or plating are to be measured. Microhardnessingeneralispressedintothesurfaceofthematerialtothetestedunderaspecificloadforadefined time interval, and a measurement is made of the size are death of the indentation[47].

FLUORESCENCE

Fluorescenceistheemissionoflightbyasubstancethathasabsorbedlightorotherelectromagneticradiation. Itisaformofluminescence.Inmostcases,theemittedlighthasalongerwavelength,andthereforelowerenergy than the absorbed radiation is in the ultraviolet radiation of the spectrum, and thus invisible to the human eye, while the emitted light is in the visible region, which gives the fluorescent substance a distinct color that can be seen only when exposed to UV light. Fluorescent material cease to glow nearly immediately when the radiation source stops, unlike phosphorescent materials, which continue to emit light for some timeafter.Fluorescence has many practical applications including mineralogy, gemology, medicine, chemical sensors, fluorescent labelling, dyes, biological detectors, and cosmic- ray detection.

IV. RESULT AND DISCUSSION
FT- IRANALYSIS

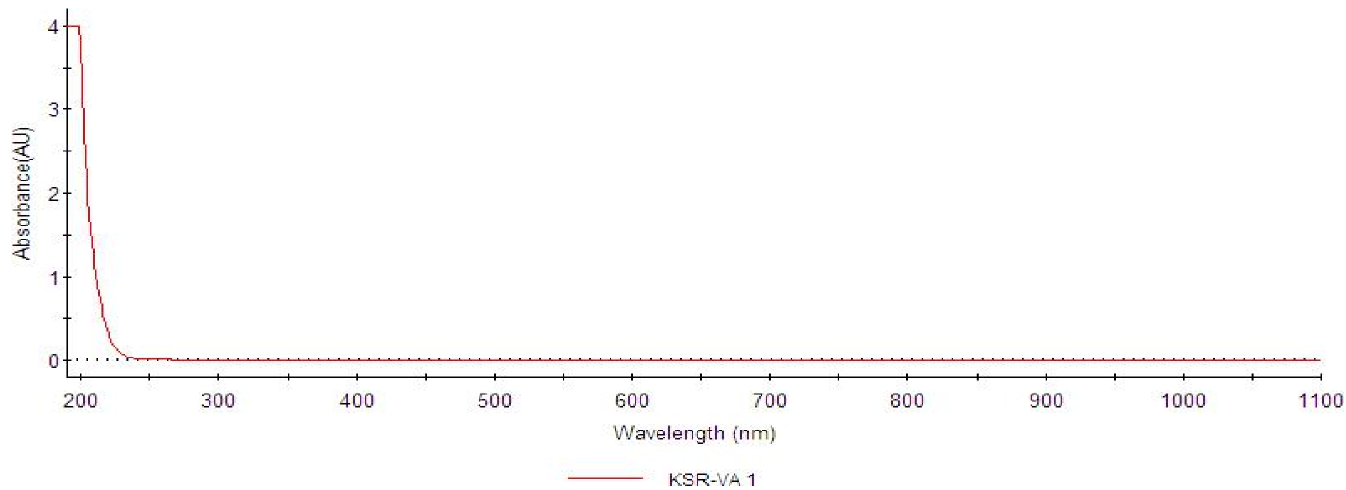
The Fourier Transform Infrared Spectrum of all the grown crystals recorded in the KBR pellet technique in the spectral range 400 to 4000 cm-1. The infrared spectral analysis is carried out to understand the chemical bonding and it period's useful information regarding the molecular structure of the compound. FTIR Spectrum ofUreaAmmoniumchloridenonlinearopticalsinglecrystalsinresolutionof0.9cm-1andwithascanningspeed of3mm/s.TherecordedFTIRspectraofasgrowncrystalsinfig.Thefollowingvibrationalassignmentsaremade and presented intable.



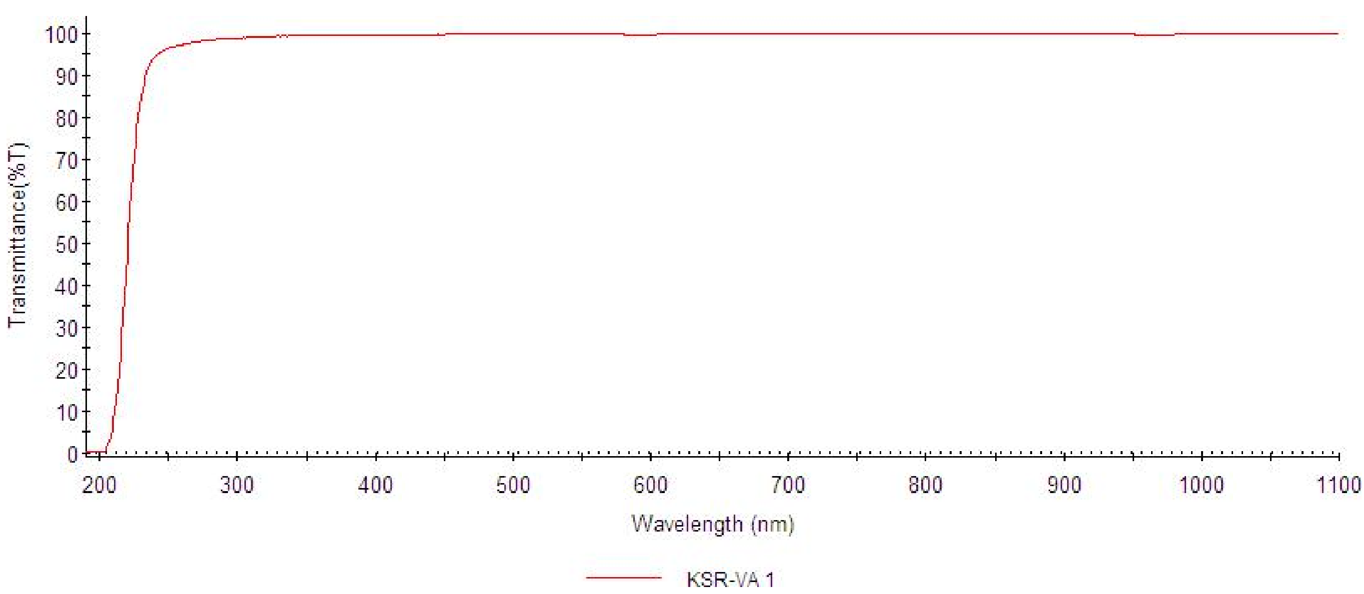
FT-IR spectra of urea ammonium chloride crystal

UV- VIS SPECTRALANALYSIS

The UV-VIS-IR transmittance spectrum was carried out using Perkin Elmer Lambda UV-VIS spectrometer in the wavelength ranging from 200-1100 nm as shown in fig (3.3). The absence of strongly conjugated bonds leads to higher optical transparency in the visible and UV spectral regions.



Optical absorption of urea ammonium chloride crystal



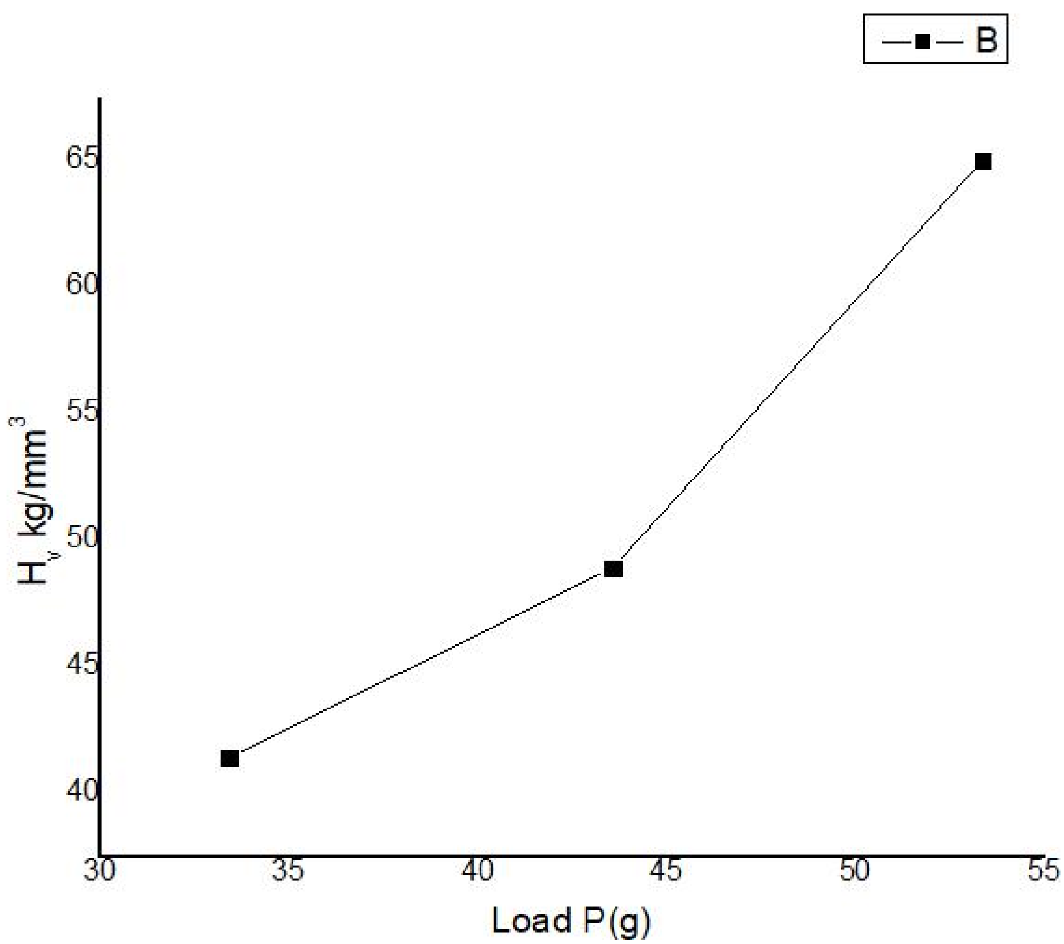
Optical Transmittance of urea ammonium chloride crystal

MICRO HARDNESSANALYSIS

Hardness of the crystal carries information about strength, molecular binding, yield strength and elastic constantofthematerial.Mechanicalstrengthofanymaterialisrepresentedbyitshardness.Hardnessofamaterial isameasureofitsresistancetothelocaldeformationcausedbyindentation.Theindentationhardnessismeasured as the ratio of applied load to the surface area of the indentation. Vicker's hardness number H_v was calculated using therelation

$H_v = 1.8544$ (P/d2) kg/mm2

Where H_v is the Vickers's micro hardness number in kg/mm2, P is the applied load in kg and d is the average diagonallengthoftheindentationinmm.Fig.3.4ShowsloadvsVickers'shardnessnumberforUreaAmmonium chloride. It is observed that the hardness increases with the increase ofload.



FLUORESCENCE SPECTRALANALYSIS

The emission spectrum of the crystal was observed from fluorescence study. These materials can be consideredforwideapplicationssincetheypossessestheintrinsicpropertiesoforganicandinorganiccompounds and their properties can evaluated through the emission spectrum.

The fluorescence spectrum of synthesized crystal was recorded using PerkinElmer (LS 45) instrument shown in fig 3.5. The crystal was exited to higher energy states by the absorption of photon energy of 99 nmand the emission spectrum was recorded in the wave length range of 250 – 800 nm. The sharp emission peak can be observed at 469 nm. The emission peak confirms that the crystal belongs to blue fluorescencespectrum.

V. CONCLUSION

Insummary,UreaAmmoniumChlorideNLOsinglecrystalsarepreparedbyslowevaporationmethod.The prepared crystal was characterized by powder XRD, FTIR, UV –Visible analysis, Micro hardness and Fluoroscenceanalysis.FromX-raypowderdiffractionstudythepeaksobserved.Fordifferentdiffractionplanes exist in the crystal were indexed and the lattice parameters were determined. The determined lattice parameter values are in –line with the literature values. Powder XRD spectrum of a grown crystals reveals monoclinic system.

The various functional group of the grown crystal were identified by FTIR spectroscopic analysis.

The UV-VIS spectrum was recorded and the absorption peak was observed around 230 nm. The largest transmittance window in the visible enables very good optical transmission of the second harmonic frequencies of Nd- YAG laser.

The Micro hardness of the crystal was absorbed that the hardness increases with the increase of load.

Theemissionspectrumofthecrystalwasabsorbedfromfluorescencestudy.Therefore,theUreaAmmonium Chloride crystal was grown and Characterization studies areobserved.

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