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Growth of urea crystals by accelerated evaporation from solution and its characterization

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ABSTRACT

Urea and its derivatives is an excellent NLO material which can be grown as crystals from solutions. There were many unfavourable conditions which imposes a limitation on the size of the grown crystal. *Urea or carbamide* with chemical formula $\text{CO}(\text{NH}_2)_2$ where the molecule has two —NH_2 groups joined by a carbonyl (C=O) functional group. Urea serves an important role in the metabolism of nitrogen-containing compounds by animals and is the main nitrogen-containing substance in the urine of mammals. It is solid, colourless, and odorless and highly soluble in water and non-toxic by nature. Dissolved in water, it is neither acidic nor alkaline. The synthesis of this organic compound by Friedrich Wöhler in 1828 from an inorganic precursor was an important milestone in the development of organic chemistry, as it showed for the first time that a molecule found in living organisms could be synthesized in the lab without biological starting materials. The terms *urea* and *carbamide* are also used for a class of chemical compounds sharing the same functional group $\text{RR}'\text{N—CO—NRR}'$, namely a carbonyl group attached to two organic amine residues. The constituents were taken in suitable containers and optimal growth conditions were designed. Urea crystallization was mooted at room temperature. After a prescribed amount of time whiskers get developed into small stick shaped crystals. Urea is also crystallized using the same solution growth technique. The crystals are analysed for their surface structural, optical and spectroscopic properties. © 2013 Trade Science Inc. - INDIA

KEYWORDS

Urea;
Crystal growth;
FTIR;
XRD.

INTRODUCTION

Urea or carbamide is an organic compound with the chemical formula $\text{CO}(\text{NH}_2)_2$. The molecule has two —NH_2 groups joined by a carbonyl (C=O) functional group. Urea serves an important role in the metabolism of nitrogen-containing compounds by animals

and is the main nitrogen-containing substance in the urine of mammals. It is solid, colourless, and odorless (although the ammonia that it gives off in the presence of water, including water vapor in the air, has a strong odor). It is highly soluble in water and practically non-toxic. Dissolved in water, it is neither acidic nor alkaline^[1]. The body uses it in many processes, the most

notable one being nitrogen excretion. Urea is widely used in fertilizers as a convenient source of nitrogen. Urea is also an important raw material for the chemical industry. The synthesis of this organic compound by Friedrich Wöhler in 1828 from an inorganic precursor was an important milestone in the development of organic chemistry, as it showed for the first time that a molecule found in living organisms could be synthesized in the lab without biological starting materials, thus contradicting a theory widely prevalent at one time, called vitalism. The terms *urea* and *carbamide* are also used for a class of chemical compounds sharing the same functional group $RR'N-CO-NRR'$, namely a carbonyl group attached to two organic amine residues. Examples include carbamide peroxide, allantoin, and hydantoin. Ureas are closely related to biurets and related in structure to amides, carbamates, carbodiimides, and thiocarbamides.

MATERIALS AND METHODS

Growth of crystals from aqueous supersaturated solutions is one of the most important methods of crystal growth. This method of low temperature solution growth producing crystals from aqueous solutions is extremely versatile in the production of many scientifically and technologically important crystals^[2]. It is also one of the most widely used methods for the growth of single crystals from solutions. Crystals can be grown by low temperature solution growth in a matter of weeks, months and sometimes years. Although this technology of growth of crystals from solution (LTSG) has been well perfected, it involves carefully planned meticulous work, high level of integrity and patience and even a fair amount of luck^[3]. A small disturbance, power failure, dust inclusion or even a contaminated batch of raw material can destroy months of hard work.

Materials having moderate to high degree of solubility in a particular temperature range, room temperature ambient to 100 °C at atmospheric pressure can be grown by low-temperature solution method. The mechanism of crystallization from solutions is governed by the interaction of ions or molecules of the solute and the solvent and crystallization which is based on the solubility of substance based on the thermodynamical parameters of the process; temperature, pressure and

solvent concentration, along with many other growth parameters^[4]. The advantages of crystal growth from low temperature solution nearer the ambient temperature results in the simple and straight forward equipment design which gives a good degree of control of accuracy of $\pm 0.01^\circ\text{C}$. Due to the precise temperature control, supersaturation can be very accurately controlled^[5]. Also efficient stirring of solutions reduces fluctuations to a minimum. The low temperature solution growth technique is well suited to those materials which suffer from decomposition in the melt or in the solid at high temperatures and which undergo structural transformations while cooling from the melting point and as a matter of fact numerous organic and inorganic materials which fall in this category can be crystallized using this technique^[6]. The low temperature solution growth technique also allows variety of different morphologies and polymorphic forms of the same substance can be grown by variations of growth conditions or of solvent. The proximity to ambient temperature reduces the possibility of major thermal shock to the crystal both during growth and removal from the apparatus^[7].

X-RAY DIFFRACTION

The structural confirmation of the grown crystal of Urea_[8] was carried out using the X-Ray powder diffraction method on the grown crystals in powdered form. The powder samples were loaded into a Rigaku X-Ray diffraction apparatus using $\text{CuK}\alpha$ radiation having $\lambda = 1.5405\text{nm}$ and examined for their peaks. Results were compared with the JCPDS database file number 99-101-0067 and ICDD 72-0118 where the prominent peaks of the reported values coincided with the in-

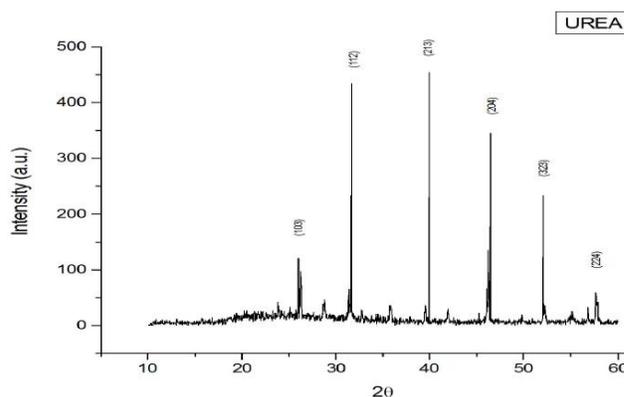


Figure 1 : Powder XRD pattern of urea crystal

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vestigated patterns. The powder XRD pattern of Urea (Figure 1) had four common prominent peaks at (112), (213), (204), (323) respectively. The cell parameters were found to be $a = 5.646 \text{ \AA}$, $c = 4.701 \text{ \AA}$ respectively. The cell volume was calculated to be 149.86 \AA^3 .

MICROINDENTATION TESTS

Microhardness tests are used to find the physical and mechanical hardness of the grown crystal of Urea where it is used to estimate the threshold mechanical stress or the maximum pressure or stress it can withstand^[9]. Samples of pure crystal of Urea and were indented using a Lietz-Wetzler P1191 Microhardness tester fitted with a Vickers pyramidal indenter with an optical angle of 136° between the opposite pyramids. Observations of the various indentation tests were done using the Metallux-II Metallurgical Microscope. A uniform indentation time of 10 seconds were applied uniformly for loads 20 to 90g. The hardness value of the as grown crystal samples (Figure 2) were found to increase slowly with the applied loads until 30g. Further application of higher loads showed that the hardness values sharply decreased and developed mild cracks on the pyramidal indentation edges. Beyond 90g the samples developed large prominent cracks due to the attainment of the threshold mechanical stress. The hardness values were calculated using the formula

$$H_v = \frac{1.8544 \times P}{D^2} \text{ kg mm}^{-2}$$

H_v is the Vickers hardness number. P is the indenter load in gm and D is the diagonal length of the impression in mm. The micro hardness value was taken as the average of the several impressions made with both di-

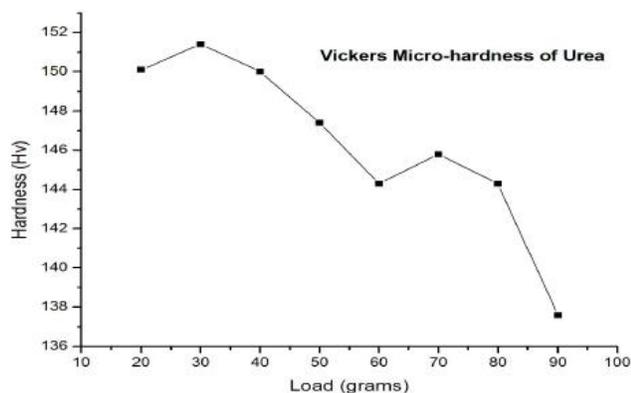


Figure 2 : Micro-indentation tests of urea crystals

agonals being measured. The variation of hardness with indenter load is shown in figure 2.

UV-VIS SPECTRAL ANALYSIS

Infrared spectroscopy is a valuable tool for both qualitative and quantitative analysis^[11]. One of the problems often encountered in applying infrared spectroscopy to quantitative analyses of solutions is the tendency for common solvents to absorb infrared light very strongly. The solvent absorptions can effectively “blank out” large regions of the spectrum, thereby blacking out valuable information about the analysed compound of interest. Water is a particularly bad solvent for use in the infrared region, as the spectral bands associated with O-H vibrations are very strong and broad. This is unfortunate, as many environmental, forensic, and clinical samples occur naturally in aqueous matrices. One way to reduce the water absorption and still obtain vibrational information is to move into the spectral region known as the near-infrared. The infrared region from $1200 - 200 \text{ cm}^{-1}$ is investigated for analysis. The spec-

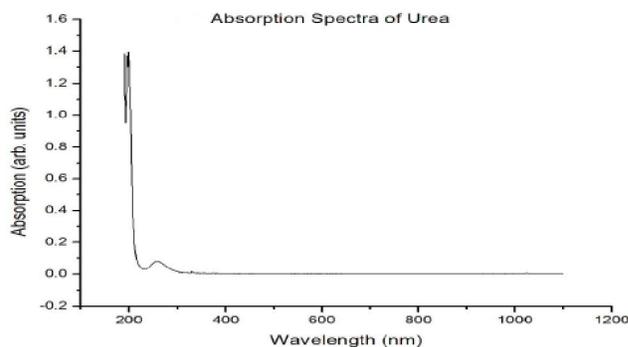


Figure 3 : UV-Vis absorption spectra of urea

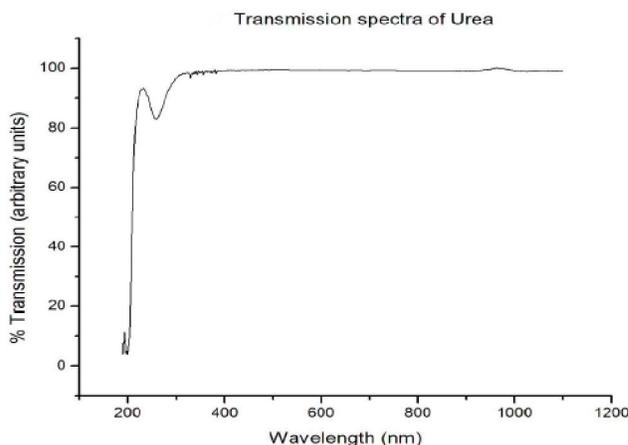


Figure 4 : Transmission spectra of urea crystal

tral bands observed in this region are overtones and combination bands associated with the fundamental vibrations found in the mid-infrared. For example, a fundamental vibration at frequency n_1 can give rise to overtone absorptions at frequencies $2n_1$, $3n_1$, etc. Fundamental vibrations at frequencies n_1 and n_2 can give rise to a combination band at frequency $n_1 + n_2$. The occurrence of overtone and combination bands is less probable than the occurrence of the fundamental vibrations, resulting in less intense bands in the near-infrared region. For example, while water still absorbs rather strongly in the near infrared, its absorption is reduced enough to allow the absorptions due to other species to be observed^[12]. There are several “windows” in the water absorption spectrum that allow many analytes to be determined directly in an aqueous matrix. The Absorption spectra of Urea was taken in a Perkin Elmer Lambda UV-VIS spectrophotometer where two prominent absorption maxima were observed at 255nm. Absorption spectra revealed that there was a good amount of transmission where the clarity of the crystal is confirmed. Transmission spectra was also taken using the same apparatus where 90-95% transmission was observed. This proves that the quality of the crystal was good and highly transparent.

FTIR INVESTIGATIONS

Fourier transform infrared spectroscopy (FTIR) is an optical technique which is used to obtain an infrared spectrum of absorption, emission, photoconductivity or Raman scattering of a solid, liquid or gas^[13]. An FTIR spectrometer simultaneously collects spectral data in a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time. FTIR has made dispersive infrared spectrometers all but obsolete (except sometimes in the near infrared), opening up new applications of infrared spectroscopy. The term *Fourier transform infrared spectroscopy* originates from the fact that a Fourier transform (a mathematical algorithm) is required to convert the raw data into the actual spectrum. For other uses of this kind of technique, see Fourier transform spectroscopy. The goal of any absorption spectroscopy (FTIR, ultraviolet-visible

(“UV-Vis”) spectroscopy, etc.) is to measure how well a sample absorbs light at each wavelength. The most straightforward way to do this, the “dispersive spectroscopy” technique, is to shine a monochromatic light beam at a sample, measure how much of the light is absorbed, and repeat for each different wavelength.

Fourier transform spectroscopy is a less intuitive

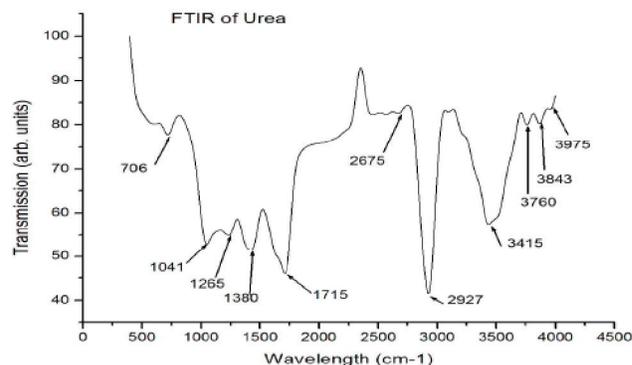


Figure 5 : FTIR investigations of urea crystal

way to obtain the same information. Rather than shining a monochromatic beam of light at the sample, this technique shines a beam containing many different frequencies of light at once, and measures how much of that beam is absorbed by the sample. Next, the beam is modified to contain a different combination of frequencies, giving a second data point. This process is repeated many times. Afterwards, a computer takes all these data and works backwards to infer what the absorption is at each wavelength. The beam described above is generated by starting with a broadband light source—one containing the full spectrum of wavelengths to be measured. The light shines into a certain configuration of mirrors, called a Michelson interferometer, that allows some wavelengths to pass through, but blocks other wavelengths due to wave interference. The beam is modified for each new data point by moving one of the mirrors; this changes the set of wavelengths that pass through. As mentioned, computer processing is required to turn the raw data (light absorption for each mirror position) into the desired result (light absorption for each wavelength). The processing required turns out to be a common algorithm called the Fourier transform. The raw data is sometimes called an “interferogram”.

FTIR spectra of the Urea (Figure 5) and doped KDP were done on a *Perkin-Elmer 781 Lambda* spec-

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trophotometer in the optimal regions 400-4000 cm^{-1} using a KBr pellet for reference. Many useful observational peaks were observed at 2675 cm^{-1} , 2927 cm^{-1} , 3415 cm^{-1} , 3760 cm^{-1} , 3843 cm^{-1} and at 3975 cm^{-1} which is in the group frequency regions (4000-1300 cm^{-1}) and the fingerprint region (1300-650 cm^{-1}). The intermediate frequency range which was between 2500–1540 cm^{-1} (*unsaturated* region) contains triple bond frequencies which appears from 2500 to 2000 cm^{-1} and double bond frequencies were found to be at 1715 cm^{-1} and which should be from 2000 to 1540 cm^{-1} . In the region between 1300 and 650 cm^{-1} there are single bond stretching frequencies and bending vibrations (skeletal frequencies) of polyatomic systems involving motions of bonds linking a substituent group to the molecule 1041 and 1265 cm^{-1} . Some of the most useful applications of infrared spectroscopy are in the area of coordination and organometallic chemistry which describes the change in the symmetry of a ligand upon coordination. For example, when small molecules (e.g. N_2 , O_2 and H_2) are linked to transition metal ions a symmetry change occurs which has a strong influence on the infrared spectra. These metal–ligand vibrations 706 cm^{-1} appear in the low frequency region (600–100 cm^{-1}) and provide direct information about the structure of the coordination sphere and the nature of the metal–ligand bond^[14]. Metal–ligand vibrations if any due to impurities are also metal sensitive and are shifted by changing the metal or its oxidation state which is applicable only to iso-structural metal complexes.

CONCLUSION

Crystal Growth of Urea by solution growth technique using the accelerated evaporation technique was carried out successfully. The Grown crystals 2mm x 20mm x 2mm were subjected to structural, optical and spectroscopic characterizations and confirmed for their properties. The growth period which was roughly two weeks time was shortened into three days at an average where very fast vaporization leads to spurious nucleation and polymerization. This is an important technique which can be successfully used in industrial crystallization.

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