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Growth of L-Arginine Acetate Crystals

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I. Abstract:- **Single crystals of pure L- Arginine acetate been grown by slow evaporation technique at room temperature. The crystalline nature of grown crystal was long-established by powder X-ray diffraction analysis (XRD). The structure of the grown crystal determined by X-ray diffraction analysis reveals that it belongs to the monoclinic system. The purposeful group of the grown crystals was establish by FTIR analysis. The UV-Vis study was performed to know the optical behavior of the grown crystals. The optical transmittance of spectrum of solid material was measured in the range of 190 to 800 nm. The crystal shows a high-quality transmittance in the visible region. The transmittance above 74% is observed from 354 to 800 nm, which clearly shows the crystal possesses good optical transparency for the second harmonic generation.**

II. INTRODUCTION

Crystals are pillars of modern technology. Modern solid-state electronics is base on a crystals growth revolution that has made possible the commercial scale growth of crystals for ferroelectrics, nonlinear optical applications, integrated circuit technology and the production of magnetic materials. Rapid advances in solid state physics over the past few decades have been responsible for the development of wide range of materials – crystals. Crystals. Crystal growth is a vital field in material science.

We can classify the crystals by the manner in which the atoms are arranged regularly. The manner of periodicity is called the symmetry of the crystals. There are three point group symmetries viz., symmetry about a point (inversion center), symmetry about a line (rotation axis) and symmetry about a plane (mirror place). Also there are two more symmetries called space group symmetries. There are compound symmetries.

i. Screw axis (Rotation + Translation)
ii. Glide plane (reflection + Translation)

The suitable combination of the point group symmetry operation gives 32 point groups. If these point group symmetry operations are combined with space group symmetry elements we get 230 space groups [1].

Neutral molecules build molecular crystals. Here the bonding is due to the Vander Wals force between them, which supplies the necessary binding energy. Most organic compounds belong to this class. Due to the comparative weakness of the bonds these crystals have low melting point [2].

Nonlinear optics is the study of interaction of intense electromagnetic fields with materials to produce modified field that are different from input field in phase, frequency and amplitude. Typically, only laser light is sufficiently intense to modify the optical properties of a material system. In fact, the beginning of the field of nonlinear optics is often taken to be the discovery of second harmonic generation by Franken and co-workers in 1961 [3].

Nonlinear optical phenomena are “nonlinear” in the sense that they occur when the response of a material system to an applied optical field depends in nonlinear manner. For example, second harmonic generation occurs as a result of the part of the atomic response that depends quadratically on the strength of the applied optical field consequently, the intensity of the light generated at the second harmonic frequency tends to increase as the square of the intensity of the applied laser light. The important nonlinear optical materials from the device point of view are generally in solid form and must meet a wide variety of ancillary material requirements for optical use. In general, they will require extraordinary stability with respect to ambient conditions and in high intensity light sources [5].

To get the good quality crystals we are in need of knowledge about the various crystal growth techniques. It is also necessary to know the need of the crystal growth, which can be stated simply as, in order to get the large specimens of crystalline material such that there is complete crystallographic continuity across a give specimen in all directions [6]. Apart from the above reason, we need to know the vital principal reasons for the deliberate grow of single crystals, which are two in number as follows,

1. Many physical properties of solids are obscured or complicated by the effects of grain boundaries.

The full of tensor relationships between applied physical cause and observed effect canbe obtained only if the full symmetry of the crystal structure is main through the specimen.

III. EXPERIMENTAL TEACHNIQUE

The solution growth is an alternative method of growth when the starting materials are unstable at high temperature. This is the simplest and oldest method of growing crystals in which the materials is to be crystallized is dissolved in water or with a suitable solvent to the desired degree of super saturation. The solution is slowly evaporated. Using a seed crystal or without seed crystal the excellent large quantity crystals can be grown.

Materials which decompose on heating or which exhibit any a structural transformation while cooling from the melting point can be grown by solution method if suitable solvents are available. This method is move widely and the growth bulk crystal. The low temperature solution growth technique is widely used for the growth of organic, inorganic single crystal to get more transparent single crystal.

Growth of single crystal from solution up to room temperature has much advantage over the other methods. Since growth is carried out up to room temperature the concentration of structural in perfect in solution grown single crystal is relatively low.

In solution growth method mainly three types are will be their

a) Slow evaporation
b) Slow cooling
c) Temperature gradient.

In the present work, slow evaporation solution growth technique is used.

MATERIAL SYNTHESIS

L-arginine acetate salt was synthesized by dissolving one equivalent amount of strongly basic amino acid, L-arginine (Lobachemie), in double-distilled water containing one equivalent amount of acetic acid. The synthesized salt was the purified by repeated crystallization until optically clear crystals were obtained. L-arginine reacts with acetic acid as follows:

$$\mathrm{(NH_2)NHCNH\,(CH_2)_3\,CH(NH_2)\,COOH + CH_3COOH}$$

$$\longrightarrow \mathrm{(H_2N)_2^{+}\,CNH\,(CH_2)_3CH(NH_3)^{+}COO^{-}\;CH_3COO^{-}}$$

CRYSTAL GROWTH

After several recrystallizations, the purified compound was dissolved in water, a saturated solution was taken and the solution was filtered solution was taken in a beaker, which was hermetically sealed to avoid the evaporation of the solvent. A good transparent single crystal of L-arginine acetate was obtained in 25-30 days. The grown crystal is shown in Fig

Figure As-grown L-arginine acetate crystals

CHARACTERIZATION OF L-ARGININE ACETATE CRYSTAL

Introduction

The Characterization of crystals is a subject in it own right and has received more attention than crystal growth. A crystal is nearly completely specified if its composition and defects are known. Characterization involves the different analysis of the chemical composition, structures and physical properties of the crystal. The characterization studies of the grown L-Arginine acetate single crystal are discussed in this chapter.

X-ray diffraction studies of L-Arginine Acetate Crystal

Introduction

Knowledge of the crystalline state of matter was decidedly limited prior to the discovery by Laue, Braggs and single crystal X-ray diffraction , that X-rays could be applied to the analysis of the internal structure of crystals. The first aim of the x-ray analysis of crystal is to determine the arrangement of atoms in the crystals and to account the properties of the crystals in terms of that arrangement. Modern X-rays methods allow determination of lattice parameters from measurements made on powdered material or single crystal method.

Determination of cell parameters

The determine the lattice parameters a, b and c, the Miller indices hkl have to be assigned. The Miller indices are defined as the reciprocals of the fractional intercepts, which the plane makes with the crystallographic axes. These integers are conventionally written in closed parenthesis, i.e., (h k l) to mean that the planes makes fractional intercepts of 1/h,1/k 1/1 with the axes. These planes have uniform spacing d_{hkl}, from the value of θ for each peak, the spacing is calculated using the Braggs law $n\lambda = 2d_{hkl} \sin\theta$ from the spectrum, lattice parameters and the interplanar distances are calculated using the following formula

***According to Bragg's diffraction equation*.**

$$2d \sin\theta = n\lambda$$

The interplanar distance, $d = n\lambda/2 \sin\theta$
Where n – is the order (n=1)

λ - is the wavelength of the monochromatic source ($\lambda = 1.5418\ A^o$)
θ - is the angle of reflection.
By knowing the value of d and β, the values of a,b,c are calculated from the relation

IV.RESULTS AND DISCUSSION

In the UV studies, the intensities in UV spectra were recorded as percentage of transmittance (%T) or as absorbance (Abs)-along y-axis and the wavelength (nm) are employed instead of wave number (per cm) –along x-axis. The absorption spectra were taken at the room temperature. The UV spectrophotometer consists of two-sample container, one was filled with double distilled water as a reference and other one was filled with the powder of grown material dissolved in water. The light beam was passed through the distilled water, which showed the 100% transmission. Another light beam was allowed to pass through the sample, if there is some absorption the ray will be deviated.

The UV-Vis analysis was made between 200 and 1200nm, which covers near-ultraviolet (200-400nm), visible (400-800nm) and then far-infra-red (800-1200) regions. The plot of % transmittance vs. wavelength (nm) and the absorbance vs. wavelength (nm) is shown in Fig.5.3. The absorbance is not registered until the wavelength 300nm is reached from 1200nm. At 245nm a sharp fall of transmittance to zero was observed indicating a single transition in the near UV region of L-arginine acetate. Absence of absorption in the region between 400 and 1200nm is an advantage as it is key requirement for materials having NLO properties [12].

THERMAL STUDIES

We know that a solid crystal is an assembly of atoms held together in a periodic array by certain binding forces. So, if we increase the temperature of the substance, There is an average increase of interatomic distance i.e., thermal expansion will takes place. Depends on temperature the materials were classified as diamagnetic, paramagnetic and ferromagnetic materials. From this we clearly understood that temperature has major role on solid-state physics. Hence the analysis of materials at different temperature is an essential factor, called thermal studies. From this thermal analysis we can locate the operating temperature range for number of applications.

Here two important methods were adopted for the analysis of the given samples they are.

1. Differential Thermal Analysis (DTA).
2. Thermo gravimetric analysis (TGA).

DIFFERNETIAL THERMAL ANALYSIS (DTA)

Differential thermal analysis has been extensively applied for qualitative and quantitative analysis of chemical compounds. This analysis found the existence of various phases which in turn to the essential studies of the formation of solid solutions. Using this technique we can record the temperature difference between a substance and a reference, when they were subjected to an identical cooling and heating process at controlled rate. This recorded out put is known as DTA curve and if the substance is thermally active, this will show a series of peaks whose positions are determined by its composition and crystal structure of the substance. The important applications of DTA are qualitative and quantitative analysis of compounds, hydration and dehydration, thermal and oxidation stabilities etc.

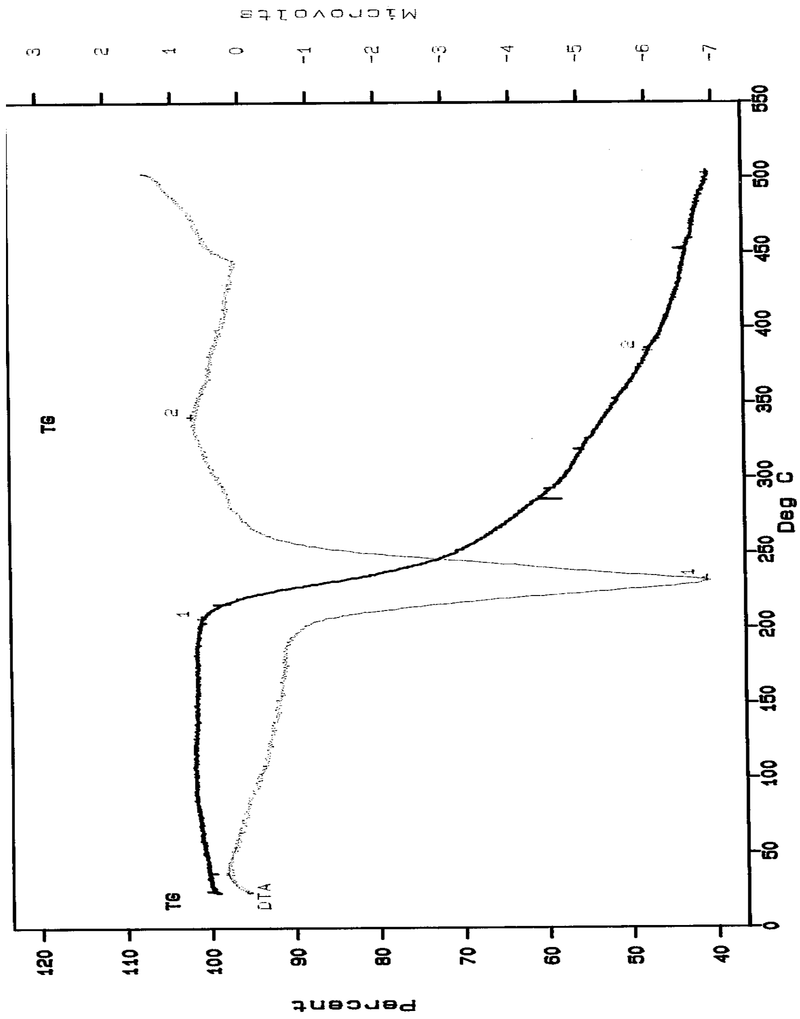
In this chapter differential thermal analysis has been extended for L-arginine acetate. From this analysis it was found that the decompositions of the materials occurred at different temperatures. The decomposition temperature for the above samples is shown in fig 5.4

Thermo gravimetric methods are largely limited to decomposition and oxidation reactions and to such physical processes as vaporization, sublimation. Thermo grams provide information about decomposition patterns of materials and weight loss also. Fig.5.4 shows the thermo gram and differential thermo gram of L- arginine acetate crystal. The analysis was performed between 25°C and 550°C at a heating rate of 5°C/min in the nitrogen atmosphere. The only one major weight loss is observed just above 200°C and 300°C. It is due to decomposition of L-arginine acetate. The formation of minute quantities of decomposition residues is also noted in the thermo gram. So from the study we conclude that the compound is thermally stable up to 200°C.

THERMOGRAVIMETRY ANALYSIS (TGA)

The Thermogravimetry Analysis (TGA) is used to record the weight loss with time or temperature due to the dehydration or decomposition of the sample. This weight loss may also due to the formation of various physical or chemical bonds at higher temperatures. Here TG analysis has been carried out and found the weight loss for L-Arginine acetate crystals.

The TGA was carried out between 25°C and 550°C in the nitrogen atmosphere at a heating rate of 10^{o}C/min. The TGA trace and differential thermo gravimetric trace are recorded in the same spectrum. The material exhibits single sharp weight loss staring at 200^{o}C. But below this temperature no weight loss is observed. Hence the crystal is completely devoid of any inclusion of water. Hence the compound is found to be stable up to 200^{o}C.



TGA analysis of the agrinine crystal

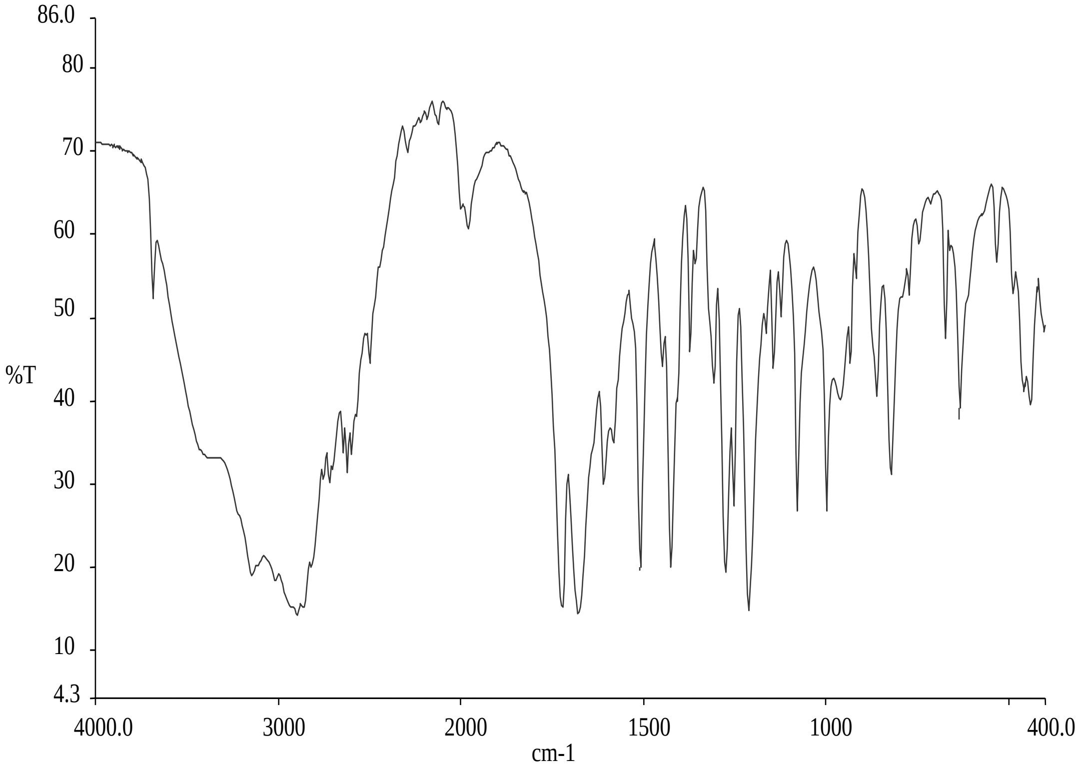
FOURIER TRANSFORM INFRARED SPECTROSFOPIC ANALYSYS

Infrared spectroscopy is the most useful tool available to the crystal grower for the solution of problems having to do with molecular behavior and the identification of unknown. Organic chemical substances and mixtures atoms of any molecule, which are molecular vibrations or motions in general, that are accompanied by a change of dipole moment during the vibration, absorb by resonance all or a portion of the radiation incident upon them, provided the frequencies of the radiation coincide exactly with the frequencies of the molecular motions.

It is not necessary that a molecule have a permanent dipole moment to absorb infrared radiation. Mono atomic atoms and icons no not usually absorb infrared radiations. All polyatomic cations and anions show absorption, however. There when an inorganic compound or complex contains anion or cation or both, infrared radiation will be absorbed. Thus borate, carbonate, nitrate, sulfate, ammonium, phosphate, cyanide, Ferro and ferri cyanide etc., show characteristic infrared absorption bands.

Fourier Transform Infrared Spectroscopy is being used mostly for the identification of organic and semiorganic compounds. The spectrum is usually a very complex and it identifies the functional group in a molecule as well as the type of bonding between various atoms. Organic molecules are not rigid, So they rather continuously undergo vibrational and rotational motions. These vibrations have certain frequencies, which are related to the masses of the atoms involved and upon the type of chemical bonding joining the atoms. This frequency of molecular vibrations corresponds to the infrared radiation. When the frequency of radiation corresponds to characteristic frequency of molecular vibration, light is absorbed. It is thus possible to identify the functional group from the appearance of the absorption bands.

The infrared region of the electro-magnetic spectrum of interest to chemist occurs rather in a narrow range, i.e.,2 microns to 15 microns (4000 cm^{-1} to 400cm^{-1}) and is capable of providing useful information. Both wavelength and frequency are commonly used to describe an infrared absorption.



In the present work, Fourier Transformed Infrared Spectra were recorded for the L-arginine acetate crystals using BRUKER 66V FT – IR spectrometer (KBr pellet technique). The recorded spectra for L-Arginine acetate crystal as shown in Fig

Interpretation of functional groups

The middle IR spectrum of L-arginine acetate was scanned between 400 and 4000cm^{-1}. The spectrum (Fig. 5.1) shows the presence of all the functional groups. The broad envelope between 2500 and 3700 cm^{-1} includes overlapping of stretching modes due to N-H and C-H. The band at 2026 cm^{-1} is due to combination of asymmetrical $-NH_3^+$ bending and vibration and its tortional oscillation. The C=O stretch of $-COO^-$ is observed at 1691 cm^{-1}. The peaks at 1501 and 1524 cm^{-1} are due to symmetric and asymmetric stretching modes of $-COO^-$ respectively. An intense absorption band appears at 3374 cm^{-1}, which is attributed to the NH stretching vibration. So, with the help of available data on the vibrational frequencies of amino acids [10], to identify the characteristic IR bands for different molecular groups present in the L-arginine acetate.

V.CONCLUSION

Optical quality bulk single crystals of L-arginine acetate crystals were grown by low temperature solution growth technique at room temperature. Single crystal X-ray diffraction studies confirm the crystallinity and shows that L-arginine acetate crystal structure is monoclinic. FTIR spectrum confirms the various functional groups present in the grown crystal. From the thermal studies, the grown crystals were thermally stable up to 200°C. Optical transmission studies show that the grown crystals were optically transparent and the lower cut off is at 245nm, and hence suitable for frequency conversion applications. The grown crystals have been subjected to single crystal X-ray diffraction studies using ENRAF NONIUS CAD4 diffractometer and its unit cell dimensions are determined. It is observed that the LAA single crystal belongs to monoclinic crystal system and unit cell dimensions a = 9.209 A°, b = 5.234 A°, c = 13.221 A°. The volume of the system is V = 637.250A$^{\circ 3}$. The observed data are in very good agreement with previous determination [9].

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