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Synthesis, growth and characterization of nonlinear optical crystal: L-arginine monohydrate

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ABSTRACT

Single crystals of L-arginine monohydrate of reasonable size and excellent quality were grown by the solution growth method. The powder XRD of the samples suggested no significant change in the unit cell dimensions and the presence of any extra phase. The structural analysis can be useful in the clarification of the role of hydrogen bonds in crystals exhibiting non-linear optical properties. The dielectric studies shows the the governance of various polarization mechanisms. The mechanical response of the crystal has been studied using Vickers microhardness technique.

Introduction

There have been significant advances in order to search and synthesize the newer acentric crystalline materials that could produce green/blue laser light. Synthesis of such materials is of great importance from both scientific and technological points of view because of their applications in opto-electronics such as frequency conversion, high-density optical data storage, optical measurements, etc. Organic materials are in increasing demand as they possess large optical nonlinearity[1-15], and they are well known for their applications in conductor, superconductor as well as innovation concerning nonlinear optical (NLO) and electro-optic device applications. Further, the binary organic materials have shown better properties for second harmonic generation (SHG) efficiency.

Although the phase diagram study and synthesis of binary materials have been an active area of investigation in metallurgy and material science, the organic systems have been studied only to a limited extent. Nonlinear optical materials capable of efficient second harmonic generation have been actively sought over the last three decades due to commercial importance [16-49]. Molecular salts composed of amino acids have been synthesised and some of these compounds show a second harmonic generation efficiency higher than urea. In this work, L-arginine monohydrate crystals were grown and subjected to various characterizations.

Solubility Studies

The L-arginine monohydrate compound was completely soluble in deionized water and acetone. The solubility studies were carried out in both the solvents from room temperature to 60^0C and the solubility curves were drawn and it is shown in Fig. 1. It was found that the magnitude of solubility was slightly more in water than acetone.

In both cases, the solubility increases linearly with temperature in the growth region. Fig. 2 shows the as grown crystal of L-arginine monohydrate with an optimized solution pH value of 3.8.

Powder X-Ray Diffraction Analysis

Powder X-ray diffraction studies were carried out using SEIFERT diffractometer with CuKα_1 (λ = 1.5406 Å) radiation to identify the lattice parameters. The diffraction data showed that the crystal belongs to Orthorombic system with Pbca space group. The unit cell parameters evaluated from the diffraction data were a = 11.470 Å, b = 9.966 Å, c = 16.0230 Å and V = 1832 $(Å)^3$ making an angle β of 90°. The crystallographic data is given in Table 1. The diffraction pattern is shown in Fig. 3. Fig 4 represents the molecular packing of the L-arginine monohydrate in the unit cell. It reveals the excellent crystallinity of the grown material.

Optical Measurements

Optical absorption was studied in the spectral range 200–1100 nm Perkin Elmer Lambda 35 UV visible spectrophotometer. The results of optical absorption studies are illustrated in Fig. 5. Optically polished single crystal of thickness 2 mm was used for this study. The optical transparency window is started from 290 nm. Hence, the present crystal may be used as Window materials in the optical lithography systems, which must withstand an intense UV laser.

Dielectric Measurements

The dielectric properties are associated with the electro-optic property of materials. Single crystals of L-arginine monohydrate of desired size were selected for dielectric measurements. They were cut and polished on a soft tissue paper with fine grade alumina powder dispersed in a mixture of acetone, water and DMFO (1:1:4). Silver paint was applied on opposite faces to make a capacitor for investigation. The sample was then mounted in a specially designed two terminal sample holder made of stainless steel. The dielectric measurements were carried out in a frequency range 100 Hz to 2 MHz at room temperature were recorded with the help of an impedance analyzer, N4L model LCR meter was used to measure the dielectric constant of the sample as the function of frequency and temperature and further automated using a computer for data recording, storage and analysis. The dielectric constant (ε_r) was calculated from the values of capacitance C using the relation

$$\varepsilon_r = Ct/\varepsilon_0 A = Ct/8.85x10^{-12} A$$

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where ε_0 is the permitivity of free space, t is the thickness of the sample and A is the area of cross section of the sample. The dielectric constant in the range of frequency 100 Hz to 2 MHz are presented at room temperature in Fig. 6.

It was observed from the plot that some significant variation in the values of dielectric constant (ε_r) with change in frequency. This nature of variation of dielectric constant with frequency indicates the governance of various polarization mechanisms.

The large dielectric constant at low frequency is contributed by space charge polarization. It is generally active at low frequencies and high temperature and indicates the perfection of the grown crystals. Thus the sway of space charge polarization is predominant in low frequency region.

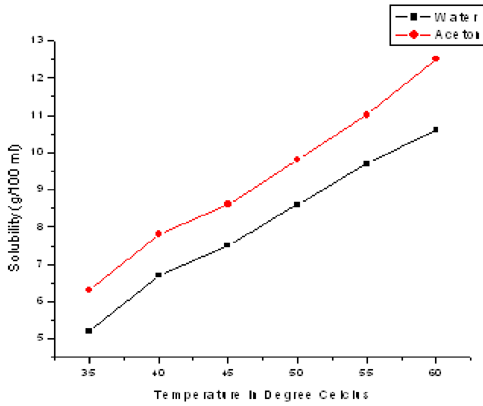

Fig.1 Solubility curves of L-arginine monohydrate

Fig.2 Grown crystal of L-arginine monohydrate

Table 1. Crystallographic data of L-arginine monohydrate

Identification code	L-arginine monohydrate
Empirical formula	$C_6H_{14}N_4O_3$
Formula weight	192.23
Crystal structure	Orthorombic
Space group	Pbca
Cell parameters	
a (Å)	11.470
b (Å)	9.966
c (Å)	16.0230
α (˚)	90
β (˚)	90
γ (˚)	90
Volume (Å)^3	1832
Z	8
Crystal size	13 x 14 x 9 mm^3

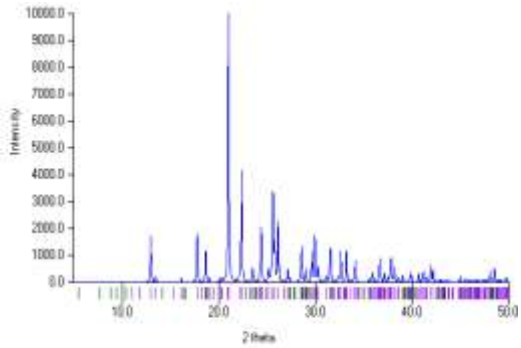

Fig .3 The XRD pattern of L-arginine monohydrate

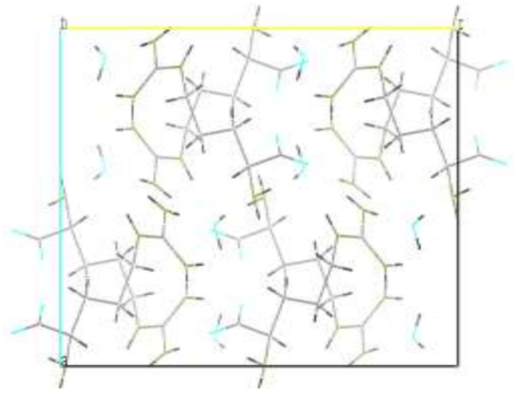

Fig .4 Packing of the L-arginine monohydrate in the unit cell

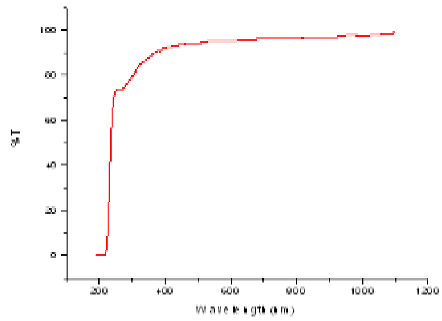

Fig..5 Optical transmission spectra of L-arginine monohydrate

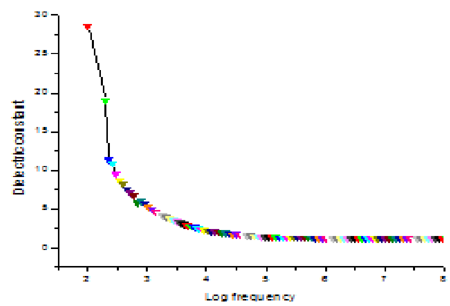

Fig. 6 Dielectric behaviour of L-arginine monohydrate

Mechanical Properties

Hardness is the resistance offered by a material to plastic deformation caused by scratching or by indentation. Fig. 7 shows the variation of mechanical behaviour of L-arginine monohydrate with applied load. In ideal circumstances, measured hardness value should be independent of applied load. But in practice, load dependence is observed. As the load is increased, there is a steep fall in hardness with load decreases and finally the hardness becomes load independent. The load variation of hardness of the type has been observed and can be interpreted in different ways. Mott et al [50] explains this type of load variation by assuming that the index of d is not 2 but less than 2. The decrease of microhardness with increasing load is in agreement with the normal indentation size effect (ISE) as observed in other works [51-54]. This supports the concept of Onitsch [55], for n<2, the microhardness decreases as load increases. At higher loads, the plastic flow of the material may be greater and hence the resistance offered by the material is negligible thus decreasing the hardness [56].

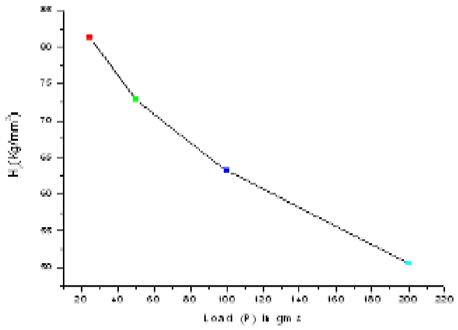

Fig 7. Mechanical behaviour of L-arginine monohydrate

Conclusion

Single crystals with good optical quality were obtained from aqueous solution by slow evaporation technique. The XRD data confirms that the crystal is orthorhombic in structure with the space group Pbca, a well-known non-centrosymmetric space group thus satisfying the requirements for second order NLO activity. From the results of optical transmission it was found that the crystal exhibit excellent transmission in entire UV-Vis range studied. Such a material could provide for a new impulse in the field of second-order nonlinear optical materials.

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