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Growth and Characterization of Single Crystals of L-argininium diiodate

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Abstract

L-argininium diiodate (LADI) single crystals had been grown by slow evaporation method using water as solvent. The structural parameters of the grown singles crystals were studied by single crystals X-ray diffraction. The various functional groups vibrations corresponding to LADI crystal were seen in FT-IR studies. The optical transparency of the grow crystals were measured by UV-Visible- NIR spectroscopy. The grown crystal mechanical stability and non-linear optical efficiency were observed through the microhardness and Kurtz and Perry tests.

Keywords: L-argininium hydrobromide, X-Ray Diffraction, FT-IR , UV-Visible- NIR spectroscopy microhardness

1. INTRODUCTION

Non-Linear optical (NLO) materials play an important role in the field of fiber optic communication and optical signal processing. Complexes of amino acids with inorganic salts are promising materials for optical second harmonic generation (SHG) as they tend to combine the advantages of the organic amino acid with that of the inorganic salts. L-arginine phosphate monohydrate (LAP) is a novel semi organic non-linear optical material whose structure was solved [1]. LAP received great deal of attention when Davydov et al. and Xu et al. reported its interesting NLO properties and thus making it a potential candidate for photonic devices [2,3]. LAP has larger nonlinearity (>1 pm=/V), higher damage threshold (>415 J/cm^2 at 20 ns), and less deliquescence when compared with potassium dihydrogen phosphate (KDP) [4–6]. Scientists have tried to grow other salts of L-arginine in view of their encouraging nonlinear properties [7–10]. A new class of arginine compounds with composition ArgU 2Ax (where Ax is an inorganic or organic acid) was reported by Petrosyan et al. [10]. This has led to the study of a series of L-arginine analogs, which exhibited interesting physical and NLO characteristics [11–16]. In the present paper, the growth and characterization of L-argininium diodate the crystal have been studied.

1. EXPERIMENTAL PROCEDURES

2.1 Synthesis

Appropriate amount of high-purity L-arginine (Merck 99%) and iodic acid with double distilled water was used to prepare the solution of LADI. The reaction is as follows:

(NH_2) NHCNH $(CH_2)_3$ CH (NH_2) COOH + $2HIO_3$

Purification is an important step in order to obtain single crystals of high quality. Hence recrystallization of the salt was carried out at least two to three times.

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2.2 Solubility

The first step in seeded solution growth is to determine the solubility of the crystal. The solubility of LADI in double distilled water was measured at six different temperatures (30, 35, 40, 45, 50 and 55 ^{o}C). The solubility data was determined by dissolving the synthesized salt of LADI in 100 ml of double distilled water at a constant temperature with continuous stirring. After attaining the saturation, the equilibrium concentration of the solute was analyzed gravimetrically. The solubility curve for LADI is shown in Figure 1.

2.3 Growth of LADI crystal

Single crystals of LADI were grown by slow solvent evaporation technique at room temperature. Saturated solution was prepared according to the solubility data using the recrystallized salt of LADI. The solution was stirred for one day using magnetic stirrer and then filtered using filter paper. The solution was then kept at room temperature to evaporate the solvent. Seed crystals of LADI were formed due to spontaneous nucleation in a period of 5-7 days. Optically clear, defect free crystals with perfect morphological faces were chosen for further growth experiment. The seeds were seasoned and then hung in the beaker containing the supersaturated solution, using a nylon thread. The optimized pH of the solution was found to be 3. Crystals of dimension 14 x 6.5 x 5 mm^3 were obtained by slow solvent evaporation at room temperature. The photograph of polished LADI crystal is shown in Figure 2. The growth period of LADI crystal was found to be 45-50 days. The optimized growth conditions for LADI single crystals is summarized in Table 4.1 The crystals obtained were non-hygroscopic, but the color of the crystal changed from transparent to pale yellow within a span of six months. As observed in the case of LADN, there was no microbial contamination in the growth solution of LADI, even when the solution was kept for more than 30 days. This may be due to the acidic nature of the solution (pH = 3). The growth habit of LADI crystal is shown in Figure 4.4. The morphology study identifies the prominent faces of crystal as (110), ($\bar{1}10$) and ($1\bar{1}0$) planes and their friedels.

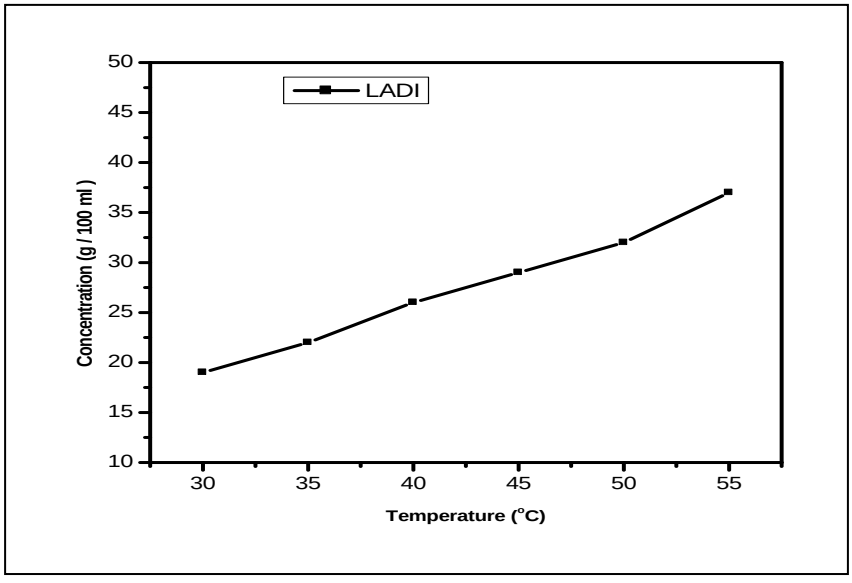

Fig 1.The solubility curve of LADI

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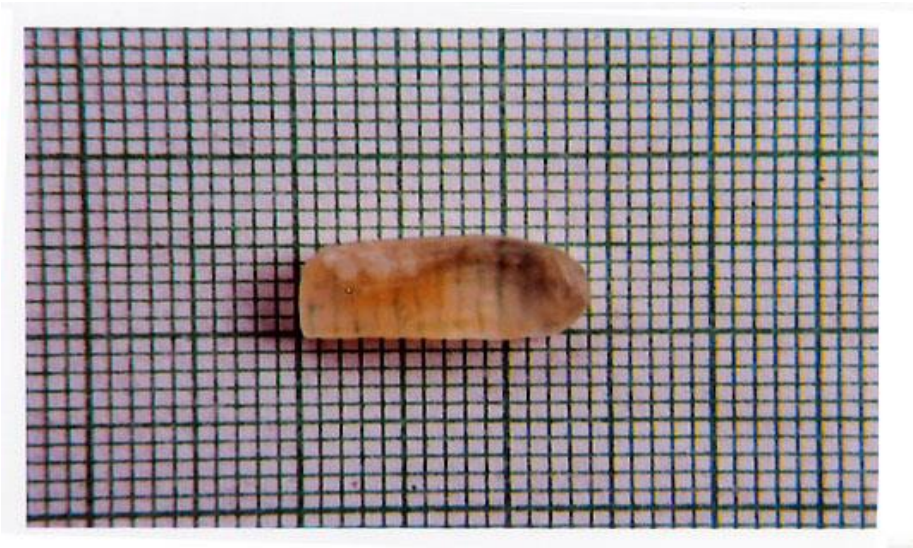

Fig .2 Photograph of the polished crystal of LADI

3. RESULTS AND DISCUSSION

3.1 Single crystal XRD

The single crystal XRD data of LADI indicates that the crystal is orthorhombic in structure with space group of $P2_12_12_1$. The lattice parameters are a = 6.9575Å, b = 7.9951 Å, c = 25.0419 Å and volume V = 1392.9833 $Å^3$. The results are in good agreement with the reported work (Petrosyan et al 2000).

3.2 Fourier Transform Infrared Spectroscopic Analysis

The middle infrared spectrum of L-argininium diiodate is shown in Figure 3. Broad strong absorption between 2100 and 3500 cm^{-1} is due to the superimposed -OH of COOH, N-H of NH_3^+, C-H of CH_2 stretching vibrations. This absorption band is characterized by multiple unresolved fine structures on the lower wavenumber side of the band. The carboxyl C=O vibration occurs at 1657.0 cm^{-1}. The asymmetrical and symmetrical NH_3^+ bends are observed at 1625.6 and 1513.0 cm^{-1} respectively. The CH_2 bends are positioned at 1445.8 and 1317.5 cm^{-1}. The C-O stretch gives absorptions at 1222.9 and 1285.0 cm^{-1}. The COO^- vibrations give a cluster of peaks between 1050 and 1200 cm^{-1}. The iodate (IO_3^-) vibrations appear between 700 and 850 cm^{-1}. The torsional oscillation of NH_3^+ occurs at 540.7 cm^{-1}.

Since the -OH stretch of carboxyl is clearly observed at 3400.6 cm^{-1}, the carboxyl group is protonated and hence, there might be two moles of iodic acid to crystallize one mole of arginine. The absence of absorption band between 600 and 700 cm^{-1} due to -OH stretch of HIO_3 confirms absence of any free HIO_3 molecule in the lattice of LADI. FT-IR frequency assignments for LADI crystal.

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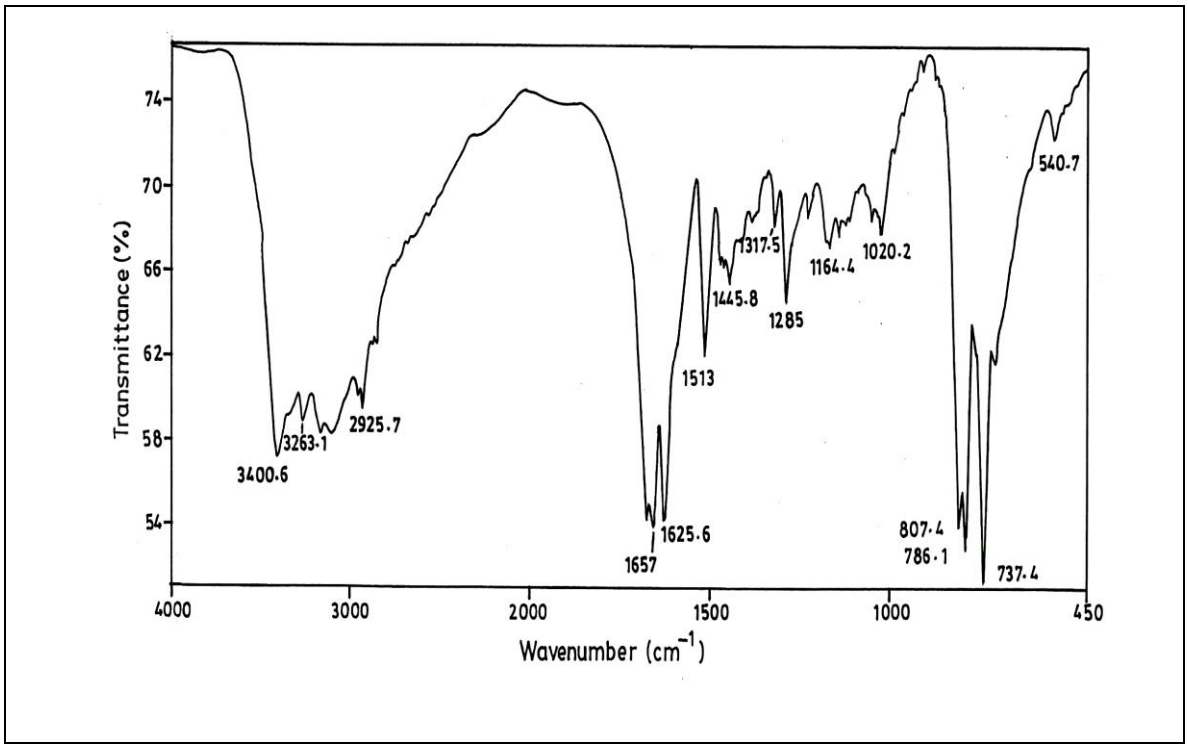

Fig 3.FT-IR spectrum of LADI single crystal

3.3 Optical Absorption Spectrum

The optical absorption spectrum of LADI was recorded using a crystal of thickness 2mm.It is evident from the spectrum (Figure 4.) that LADI has its cut-off wavelength around 250 nm. LADI has a low value of cutoff wavelength when compared with LAF and LAD (Haja Hameed et al 2003;), but the value is greater when compared with LAHCl and LAHBr. The absorbance is found to be nearly equal to zero in the entire visible region, which is a desirable property of the crystals used in NLO applications.

3.4 Micro hardness Studies

Microhardness studies have been carried out on the (110), $(1\bar{1}0)$ and $(\bar{1}10)$ planes. A graph has been plotted between hardness number (H_v) and applied load (p) for the corresponding planes (Figure 5). It is observed that the (110) plane is harder (H_v = 160.7 kg/mm^2) than the other two planes. It is seen from the graph that the H_v number for (110) plane increases linearly with applied load upto 30 gm. Beyond that microcracks are observed and further measurements are not possible. The microhardness studies further confirm that among the various analogs of LAP reported so far, LADI has the highest value of Vickers Hardness Number (H_v = 160.7 kg/mm^2). The H_v values of other analogs of LAP.

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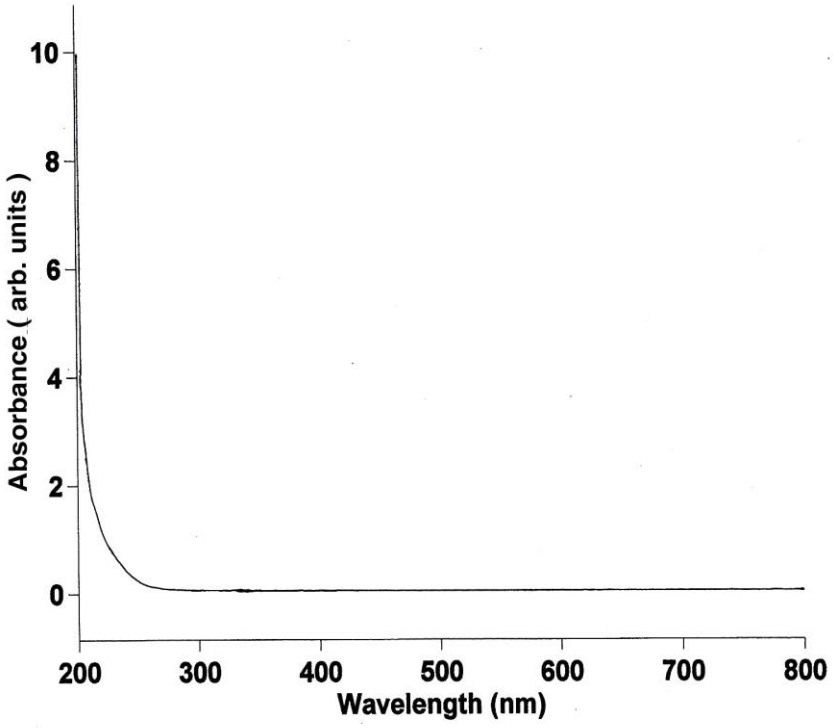

Fig 4. Optical absorption spectrum of LADI single crystal

The reverse type of indentation size effect, in which the apparent microhardness increases with increasing applied test load, has been critically examined for a number of single crystals. This reverse ISE has been explained in terms of the existence of a distorted zone near the crystal-medium interface, effects of vibration and indenter bluntness at low loads, the applied energy loss as a result of specimen chipping around the indentation and the generation of median or radial cracks during the indenter loading half-cycle.

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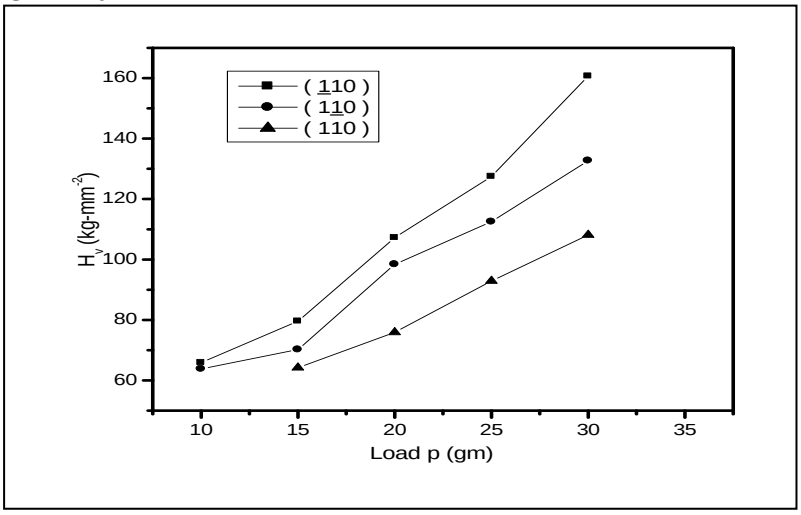

Fig .5 Variation of Vickers Hardness number with load on (110), ($\bar{1}10$) and ($1\bar{1}0$) orientations of LADI single crystal

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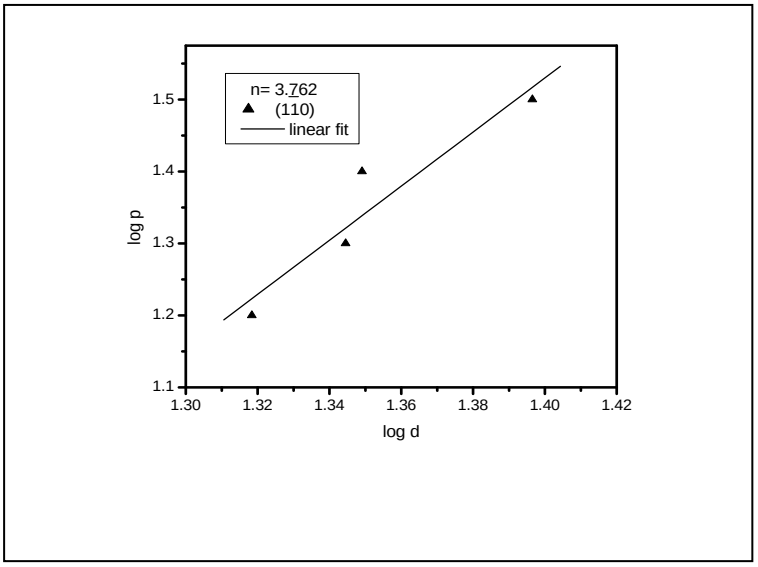

Fig .6 Meyer's plot on the ($1\bar{1}0$) plane of LADI crystal

In the case of reverse ISE, a specimen does not offer resistance or undergo elastic recovery, as postulated in some of the models, but undergoes relaxation involving a release of the indentation stress along the surface away from the indentation site. This leads to a larger indentation size and hence to a lower hardness at low loads. It was also found that the reverse ISE phenomenon occurs only in materials in which plastic deformation is predominant.It was found that, in the case of crystals exhibiting reverse ISE, the value of Meyer's index n is greater than 2. Figure 6 shows the plot of log p against log d for ($1\bar{1}0$) orientation of LADI single crystals. The Meyer's number (n) for this kind of reverse ISE, as expected was found to be 3.762 for the above plane

CONCLUSION

Optically good grade single crystals of LADI were grown using slow solvent evaporation technique. FT-IR analysis it was proved that there might be two moles of iodic acid to crystallize one mole of L- arginine. It is evident from the optical absorption spectrum that the absorbance is found to be nearly equal to zero in the entire visible region. The microhardness study further confirms that among the various analogs of LAP reported so far, LADI has the highest value of Vickers hardness number (H_v = 160.7 kg/mm^2).

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