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Structural and Spectroscopic Characterization of L-Arginine Phosphate (LAP) Crystals

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ABSTRACT

High quality bulk single crystal of L-arginine phosphate (LAP) was grown by slow evaporation which is based on temperature reduction method. L-arginine phosphate (LAP) seed crystals were grown at pH value of 5.8 at 30^0 C by slow evaporation technique around 12 days and the bulk crystal was grown by Mason-jar method for 20 days. The grown crystals were subjected to optical and morphological studies. The unit cell parameters were calculated by X- ray diffraction. The UV-Vis spectrum shows the transmitting ability of the crystals in the entire visible region and the transmittance percentage is increased for the LAP crystals. The presence of the functional groups was identified by FT-IR spectrum. Hence L-arginine crystals are found to be more beneficial from an application point of view as compared to KDP crystals. From Micro hardness test the mechanical strength of the crystal has been observed.

Introduction

L-arginine phosphate (LAP) is an organic nonlinear colourless optical material [1]. It is optically biaxial [2] and monoclinic in structure. It is an excellent crystal for second harmonic generation [3] because of its high conversion efficiency.

We have investigated various growth techniques to obtain the bulk LAP crystal and found that, defect-free seed crystals of LAP can be grown by dissolving commercial L-arginine Phosphate in deionised water [4]. The bulk single crystal can be grown by slow isothermal solvent evaporation technique using Mason jar.

Synthesis

L-arginine phosphate (LAP) seed crystals were synthesized from aqueous solution by slow cooling as well as by slow evaporation methods. The slow evaporation technique is mainly used for synthesizing seed crystals [2].

The solution was prepared by dissolving commercial L-arginine phosphate in deionised water. It is well known that both pH and temperature have influence on growth of crystal. In order to investigate the effect of pH on growth of crystal in lab experiment were carried out at pH value of 5.8 at 30^0 C. Before the actual growth, L-arginine phosphate (LAP) seed crystals were recrystallized several times for purification purpose. L-arginine phosphate (LAP) seed crystals were grown by slow evaporation for 12 days and bulk crystal were grown in Mason jar around 20 days.

The best growth condition was determined based on the thickness, its transparency and morphology of the crystal obtained. Bulk transparent crystal of L-arginine phosphate (LAP) was obtained at higher concentration.

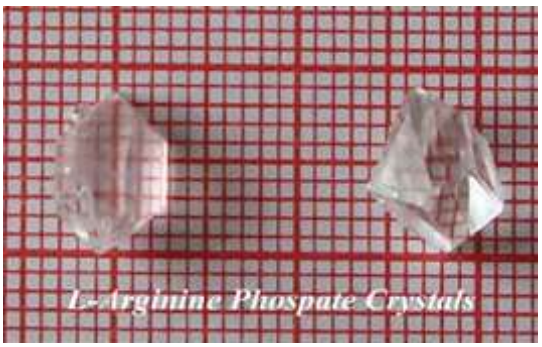

Figure 1. Bulk Single crystals of L-Arginine Phosphate

Characterization

XRD diffraction studies

Powder X-ray diffraction studies of L-arginine phosphate crystals were carried out using XPERT PRO diffractometer with CuKα (λ = 1.5418 Å) radiation. The samples were scanned for 2θ values from 10°–80° at a rate of 2°/min. Fig 1 shows the powder XRD pattern of the LAP crystal. The powder patterns were indexed and the lattice parameter values for the LAP crystal were calculated. It is observed that LAP crystal was crystallized in monoclinic P21 space group. The lattice parameters of the samples are a = 10.89 Å, b = 7.912 Å, c = 7.342 Å, α = β = γ = 90° and Volume (V) = 627.18 $Å^3$ were determined from the collected X-ray data and they were matched well with the literature value. There are slight variations in the lattice parameters and cell volume of the L-arginine phosphate.

FT-IR studies

The FT-IR spectrum of L-arginine phosphate crystals have been recorded within the wave number range 400 cm^{-1} to 4000 cm^{-1}. Pellets with the constituents of each sample with KBr have been prepared and used in the experiment and the spectral result has been shown in the Fig 3. In the FT-IR spectra of LAP crystal, the observed absorption peaks corresponding to the P-

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OH stretching, P-O-H bending, C = O stretching and CH_2 bending based on the chemical structure the frequency assignments have been made to establish the functional groups present in the grown crystal and as nearly to the literary values [5]. The L-arginine phosphate (LAP) exhibits the peak at 3170.23 cm-1 is due to asymmetric stretching of NH_3. The band at 1650.68, 1524.92 cm^{-1} is due to asymmetric stretching of NH_3 symmetric stretching of NH_3. The band at 1409.33 cm^{-1} is due to symmetric stretching of C-COO. The band at 1130.61 is due to NH_3 Rocking and 614 cm^{-1} is due to O-H bending.

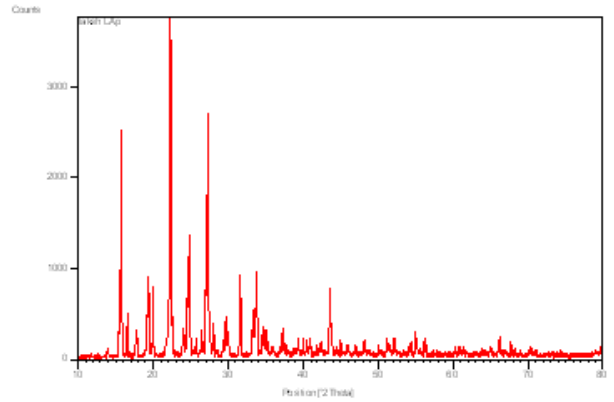

Figure 2. XRD analysis of L-Arginine Phosphate

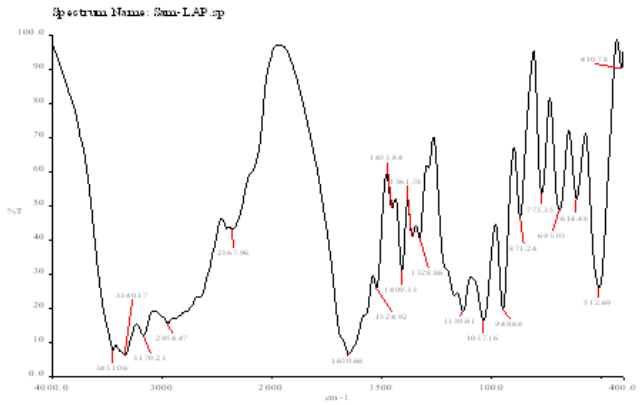

Figure 3. FT-IR spectrum for L-Arginine Phosphate

Table I. FT-IR peak Assignments

S.No	LAP	Assignments
1	3170.23	NH_3 asymmetric stretching in amino salt
2	2954.47	CH Stretching mode, to CH_2 stretching
3	1650.68	NH_3 asymmetric deformation
4	1524.92	NH_3 symmetric deformation
5	1409.33	Symmetric stretching of $C\text{-}COO^-$
6	1361.78	C-C-H in plane deformation
7	1130.61	NH_3 Rocking
8	614.48	O – H Bending

Microhardness studies

The micro hardness of the material was measured by using the Vickers diamond pyramidal indentor attached to a REICHERT POLYVAR 2 MET microscope. The micro hardness measurements were made for the applied loads varying from 25 to 100 g. The hardness of the crystal can be calculated using the relation

$Hv = 1.8544\ p / d^2$

Where Hv is the Vickers hardness number,

p is the indenter load in gm

d is the diagonal length of the impression in mm

The hardness of the L-Arginine Phosphate crystal has been shown in the Table. II

Table II. Hardness Measurement

S. No	Compound	Load		
		25gms	50gms	100gms
1	LAP	30.69	40.62	54.46

At lower loads there is an increase in the hardness with load, which can be attributed to the work hardening of the surface layers. At higher loads the microhardness shows a tendency to saturate. At 100 grams of load, significant cracking occurs for LAP. This may be due to the release of internal stresses generated locally by indentation.

UV-Visible spectral studies

The optical properties of a material are important, as they provide information on the electronic band structure, localized state and types of optical transitions. L-arginine phosphate crystals plates with a thickness of 2mm without antireflection coating were cut and used for optical measurement. The UV-Visible transmission spectrum was recorded using Perkin Elmer Model-Lambda 35 spectrometer in the range 190nm to 1100nm.

From the graph, it is evident that the LAP crystal has a transparency window from 210nm onwards suggesting the suitability for SHG of the 1064nm radiation. The LAP crystal has good transmission in the entire visible region. The optical losses in the higher wavelength side could also be reduced by optimizing the growth conditions towards the production of crystals of higher quality. The large transmittance window in the visible region enables very good optical transmission of second harmonic frequencies of Nd:YAG lasers.

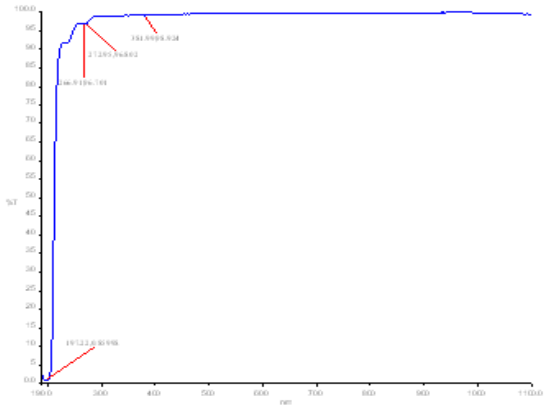

Figure 4. UV-Visble Absorption spectra for L-Arginine Phosphate

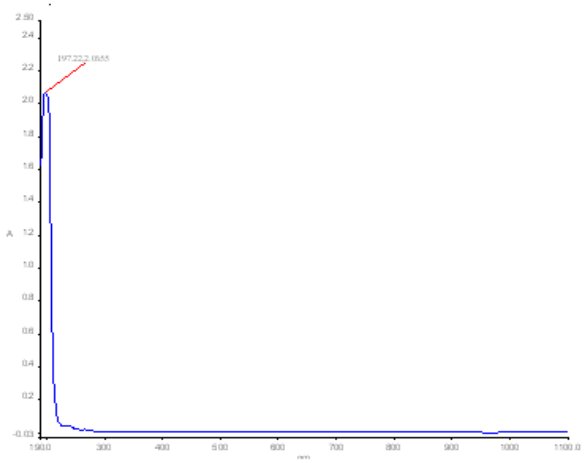

Figure 5. UV-Visble Transmission spectra for L-Arginine Phosphate

Conclusion

Single crystals of LAP were grown by slow solvent evaporation technique in a period of 15 days. XRD study was

carried out to determine the cell parameters. Crystal structure analysis shows that LAP crystal belongs to a monoclinic system. FTIR spectrum confirmed the functional groups present in the grown crystal. The micro hardness shows that, at 100 grams of load, significant cracking occurs for LAP. Optical transmission studies show that the crystal has a wide transparency range with a lower cut-off of 210nm. UV-Vis spectrum revealed that the LAP crystal is transparent in the entire visible region. With wide transparency range and high second harmonic efficiency, the LAP crystal can be used for NLO device applications.

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