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Growth and characterization of l-arginine diphospate single crystals

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ABSTRACT

The experimental results of optical, mechanical, electrical and photoconductivity studies of nonlinear optical crystal L-arginine dinitrate (LADN) are presented. Good optical quality single crystals with dimensions up to $11 \times 7 \times 6$ mm^3 were obtained. LADN has a wide optical transmission window between 251 and 1200 nm. Its optical damage threshold and SHG efficiency is comparable with that of KDP.

1. INTRODUCTION

L-arginine is one of the essential amino acids widely distributed in biological substances. It is also the most basic of the amino acids, since in addition to the α-amino group; it also contains a terminal guanidy1 group[1]. The strong basicity of the guanidy1 group is responsible for the functions in living matter[2]. L-arginine phosphate monohydrate (LAP) is found to exhibit interesting non-linear optical properties[3]. The importance of amino acids in NLO applications are due to the fact that all the amino acids except glycine contain chiral carbon atom and crystallize in non-centrosymmetric space groups. The introduction of L-arginine phosphate monohydrate (LAP) has played an important role both in the crystallization of new salts of amino acids and in the development of semi-organic crystals.

Recently, Reena and Sagayaraj[4] (2002) reported on the growth of L-arginine diphosphate (LADP) by slow solvent evaporation technique. Owing to its good transparency, chemical stability, dipolar strength, L-arginine diphosphate seems to be a promising material for NLO application. The present work deals with the growth habits and characterization of pure LADP crystals. The crystals grown from aqueous solution of LADP were subjected to various characterization studies to understand the structural, crystalline nature, mechanical and photoconduction properties.

2. EXPERIMENTAL

2.1. Synthesis and solubility

Appropriate amount of L-arginine and orthophosphoric acid were dissolved in double distilled water to synthesize LADP. The required amount of L-arginine was dissolved in 100ml of millipore water. The stoichiometric amount of phosphoric acid was slowly added to it. In the present work, water is used as a solvent. Due to the relatively high solubility of LADP in it (45gm / 100 ml of water at 30^0C) and the favorable thermal coefficient of solubility, water evaporates and produces seed crystals. After two weeks, the defect free and transparent seed crystals of LADP were selected and used for the growth experiment. Single crystals of size $11\times 7 \times 6$ mm^3 are grown in a period of 50-60 days using the Manson Jar Crystallizer.

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The solubility of pure LADP in water has been determined for four different temperatures, 30, 35, 40 45 and 50°C respectively (Figure 1). A 250 ml glass beaker covered with a rubber cork was used as nucleation cell. The nucleation cell was kept on the platform in a constant temperature bath, which controls the temperature with an accuracy of 0.01^0C. After achieving the saturation, the content of the solution was analyzed gravimetrically. Figure 2 shows the photograph of as grown LADP crystal grown by slow evaporation method. The crystals are non-hygroscopic and optically transparent.

The morphology of pure LADP crystal is shown in figure 3. LADP crystal grows as a polyhedron with ten visible faces of which three are on the top and three on the bottom. The crystals are very long in the 'a' direction (shortest crystallographic axis). The main trunk of the crystal has four faces, with planes (0 1 $\bar{2}$), (0 1 2) and their friedels. The planes (1 0 0), (0 1 0) and (0 0 1) are not morphologically developed. The three faces on one end of the crystal are (1 1 0), (1 $\bar{1}$ 0) and (1 0 1). In Figure 3, PQ, which is the edge of the intersection between the adjacent faces (1 $\bar{1}$ 0) and (1 $\bar{1}$ 0) should be the c direction. b which should be normal to **a** and **c** is not a developed edge or direction.

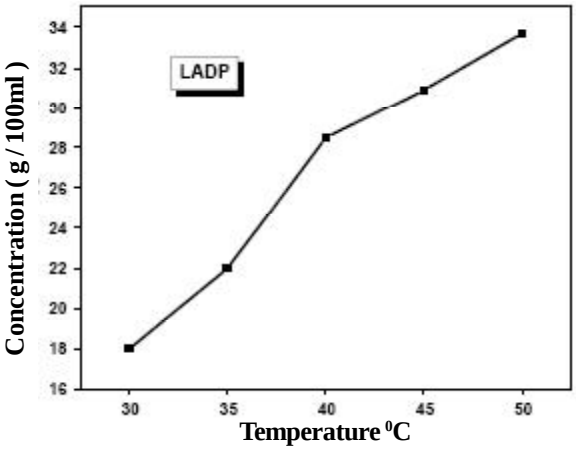

Figure 1 : Solubility curve of LADP crystal

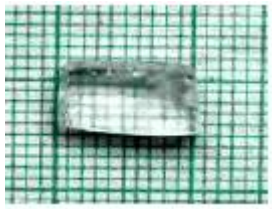

Figure 2 : Photograph of as grown LADP single crystal

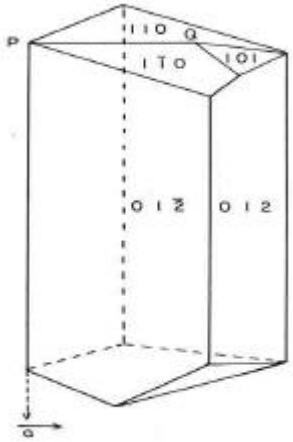

Figure 3 : Morphology of pure LADP crystal

RESULTS AND DISCUSSION

3.1. Single crystal XRD analysis

The pure LADP single crystals were analyzed by single crystal X-ray diffraction method. A single crystal specimen of suitable size was cut from a large crystal of the title compound. The single crystallinity was tested using a Leica polarizing microscope. The X-ray data were collected on an automatic X-ray diffractometer (MESSRS ENRAF NONIUS, The Netherlands). The structure was solved by the direct method and refined by the full-matrix best-squares technique using the SHELXL program. The calculated lattice parameter values are presented in TABLE 1. It is observed that, pure LADP crystals have orthorhombic structure with a space group of $P2_12_12_1$. The lattice parameter values of pure LADP are in good agreement with the reported work[5].

TABLE 1 : Crystal data for LADP crystal

Crystal system	Present work
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a(Å)	6.991(2)
b(Å)	9.676(5)
c(Å)	21.735(2)
Volume Å^3	1470.26 (3)
Z	4

3.2. CHN analysis

For identifying the synthesized material, the CHN analysis was employed along with FT-IR and single crystal X-ray diffraction (XRD) analyses. The elemen-

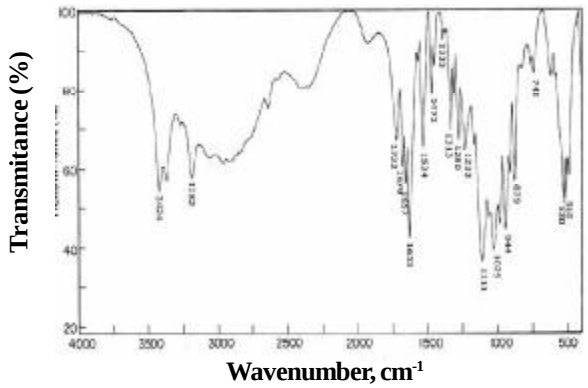

Figure 4 : FT-IR spectrum of LADP crystal

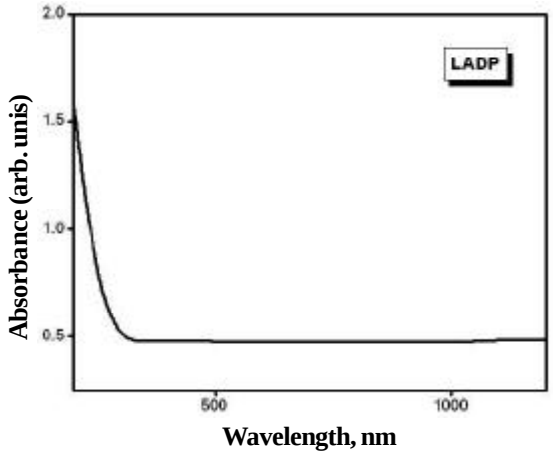

Figure 5 : Optical absorption spectrum of LADP crystal

TABLE 3: FT-IR frequency assignments for LADP single crystal

Wave number (cm^{-1})	Assignment
3424	N-H asymmetric stretching
3182	N-H stretching
1722, 1679	C=O stretching
1657	N-H bending
1633	NH_2 deformation
1534	NH_3^+ symmetric deformation, NH_2 in-plane deformation
1473	CH_2 in plane deformation
1333	CH_2 wagging
1313	C-N stretching
1280	P=O stretching
1233	P=O stretching
1111	γ (PO_4)
1025	C-O stretching
944	CH_2 Rocking
879	C-C stretching
743	NH_2 out of plane bending
530	γ (PO_4)
510	P-OH deformation

tal analysis of LADP was performed using Elementar Vario EL 111 Elemental analyzer. The theoretical and experimental atomic weight percentages are summarized in TABLE 2. Thus the chemical composition of LADP is established.

TABLE 2 : Results of elemental analysis of LADP crystal

Molecular weight: 277.193 g/mol		
Elements	Weight % composition	
	Theoretical	Experimental
C	21.665	22.010
H	6.545	6.783
N	20.212	20.009

3.3. FT-IR analysis

The FT-IR spectra of pure LADP crystals were recorded on BRUKKER IFS FT-IR SPECTROMETER using KBr pellet in the range 4000 cm^{-1} to 400 cm^{-1} and are shown in the figure 4. The frequency assignment of these crystals is presented in TABLE 2. From the FT-IR spectrum, it is concluded that phosphoric acid is bonded to L-arginine through ionization. A peptide bond CO–NH is formed between the carboxyl group COOH in L-arginine and it is clearly visible in the spectrum between 1600 cm^{-1} and 1750cm^{-1}.

3.4. UV-Vis- NIR study

The optical absorption spectra of LADP single crystals were recorded in the region 200 nm to 1200 nm using Varian Carry 5E model spectrophotometer. Figure 5 shows the optical absorption spectra for the crystal. The minimum absorbance lies between 251 nm and 1200 nm, which enable the material to be a good candidate for NLO applications.

3.5. Nonlinear optical (NLO) study

Kurtz SHG test was performed on LADP crystal to confirm the second harmonic signal generation efficiency. Microcrystalline sample of KDP was used as a comparison with LADP, for the SHG experiments. For a laser input pulse of 6.2 mJ, the second harmonic signal (532 nm) of 91.66 mV and 294 mV were obtained through KDP and LADP samples respectively. Thus the SHG efficiency of LADP is 3.2 times that of KDP. The SHG efficiency of LADP is less than LAP[6], but greater when compared with some of the analogs of LAP.

3.6. Laser induced damage threshold study

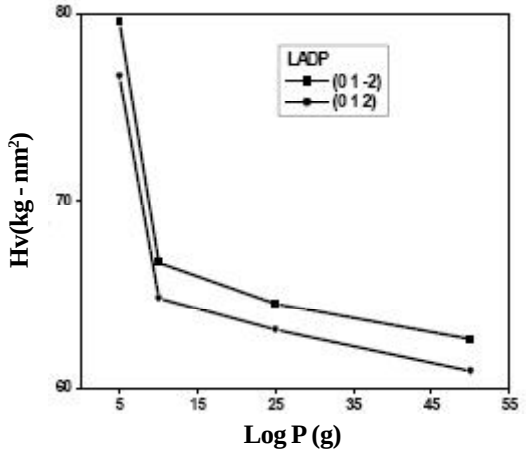

Figure 6 : Variation of vickers hardness number with load

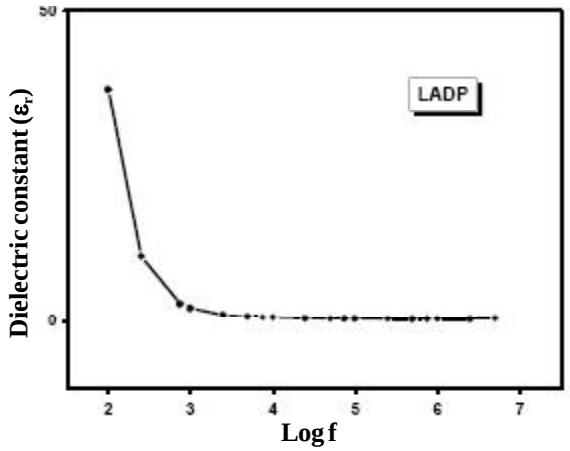

Figure 7 : Variation of dielectric constant with frequency

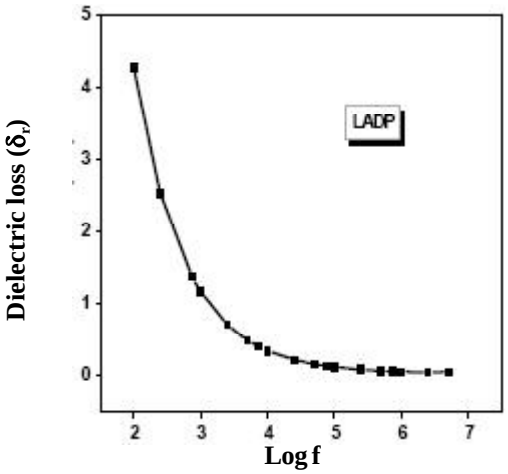

Figure 8 : Variation of dielectric loss with frequency

In this section the results of laser induced damage threshold studies performed on LADP are presented. The laser damage threshold of LADP was carried out using laser setup in a single shot mode and it was found to be about 9.1 GW / cm^2, which indicates the suitability of this crystal for NLO applications.

3.7. Microhardness studies

Microhardness studies have been carried out on pure and doped LADP single crystals using a Leitz Wetzlar Vicker's microhardness tester. The static indentations were made at room temperature with a constant indentation time of 10 seconds. For pure LADP, the indentation marks were made on the (0 1 2) and (0 1 $\bar{2}$) planes by varying the load from 5 to 50 gm. Above 50 gm micro cracks were observed and hence readings were not taken for higher loads. The variation between hardness number (Hv) and the applied load p for the two planes (0 1 2) and (0 1 $\bar{2}$) of the pure crystal and is shown in figure 6. It is observed from the plot that the hardness number decreases as the load increases.

3.8. Dielectric studies

The dielectric study for the crystal was carried out on the (0 1 2) plane. Figure 8 and 9 shows the variations of dielectric constant and dielectric loss of LADP crystal at temperature of 308 K, as a function of log frequency. From figure 7 it is seen that the value of dielectric constant becomes independent of frequency in the high frequency region. The dielectric constant is found to decrease with increase in frequency in the low frequency region. It is observed from Figure 8 that the value of dielectric loss decreases with frequency, and it becomes independent of frequency in the high frequency region. The low value of dielectric loss at high frequency can be taken as a proof for the good optical quality of the crystal[7].

3.9. Photoconductivity studies

Photoconductivity of pure LADP crystals was studied using Keithley 480 picoammeter. Both dark conduction and photoconduction were studied. Conductivity measurements were carried out on the sample by fixing electrodes using silver paint. Dark conductivity of the sample was studied by connecting the sample in series to a DC power supply and a picoammeter. Electrical contacts were made at spacing (d) of about 2 mm on the sample using silver paint. The DC input was increased from 0 to 300 volts in steps and the corre-

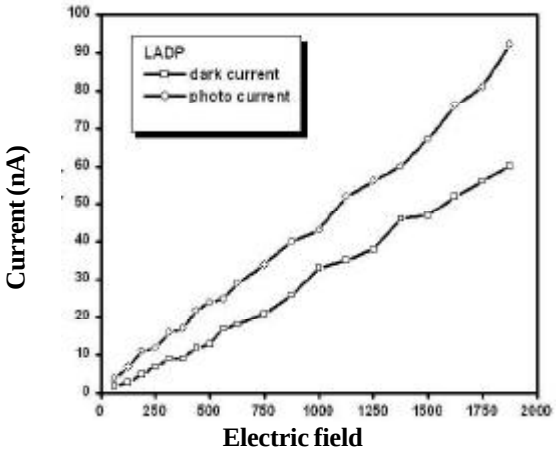

Figure 9 : Variation of dark and photo current with applied field

sponding readings in the picoammeter were taken for pure LADP crystals.

The variation of dark current (I_d) with the applied field (E) is measured by increasing the applied field from 62.5 V/cm to 1875 V/cm for pure LADP crystal. The dark current vs applied field plot indicates that I_d increases with increasing values of the applied field (Figure 9). The variation of photocurrent (I_p) with the applied field is also shown in the same plot. It is observed from the plot that the photoconductivity is more than the dark current, for the same applied field. Thus, the LADP crystal exhibits positive photoconductivity.

4. CONCLUSION

Good quality LADP single crystals were grown by the slow solvent evaporation technique. X-ray diffraction data confirmed that LADP crystal is orthorhombic in structure belonging to the space group $P2_12_12_1$. The optical absorption spectrum shows that maximum absorbance for the crystal lies between 251 and 1200 nm. From the FT-IR spectrum, it is concluded that phosphoric acid is bonded to L-arginine through ionization. The thermal stability of LADP is found to be much higher than that of L-arginine monophosphate (LAP). The microhardness studies indicate the anisotropic nature of the hardness values for pure LADP crystal. Pure LADP crystal exhibits positive photoconductivity.

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