

## Optical and thermal studies on pure and doped L-arginine phosphate crystals

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### Abstract

In the present study the single crystal growth of the pure and doped organic nonlinear optical crystal, L-arginine phosphate is reported. The dopants used were urea and thiourea. The crystals were grown by slow evaporation technique. The presence of various functional groups in the grown crystal was confirmed by Fourier transform infrared (FT-IR) analysis. The thermal properties of the grown crystals were studied by thermo gravimetric and differential scanning calorimetry analysis (TG/DSC). Second harmonic generation (SHG) measurement was used to confirm the organic nonlinear optical properties of the grown crystal.

**Keywords:** Growth from solutions; nonlinear optical materials; thermal analysis; doped LAP.

### Introduction

Organic nonlinear optical (NLO) materials attract a great deal of attention due to their applications in optical devices, such as optical switches, optical modulators, optical communications, optical data storage etc. (Wong *et al.*, 1996; Dmitriev *et al.*, 1999; Gnanasekaran & Madhavan, 2008; Munirathnam & Madhavan, 2009). Among the organic class of compounds,  $\alpha$ -amino acids exhibit some specific features such as molecular chirality, weak Van der Waals and hydrogen bonding, the absence of strongly conjugated bonds, wide transparency ranges in the visible and UV spectral regions and zwitterionic nature which favours crystal hardness (Nicoud & Twieg, 1987). L-arginine phosphate [L-Arg: $\text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ , L-Arg. is  $\text{NH}_2\text{C}(\text{NH})\text{NH}(\text{CH}_2)_3\text{CH}(\text{NH}_2)(\text{COOH})$ , abbreviated as LAP] has been found to be a very promising NLO material (Xu *et al.*, 1983). L-arginine phosphate (LAP) crystals can be grown from aqueous solutions. It is a biaxial crystal and belonging to the monoclinic system with space group  $P2_1$ . The lattice parameters are  $a = 10.75 \text{ \AA}$ ,  $b = 7.91 \text{ \AA}$ ,  $c = 7.32 \text{ \AA}$  and  $\beta = 98^\circ$ . Salient features of LAP that make it a better choice in NLO applications are wide transparency range, high optical damage threshold power, high non linear optical coefficient ( $>1\text{pm/V}$ ) and less hygroscopic nature than KDP crystals (Dhanraj *et al.*, 1991; Ravi *et al.*, 1994). In the present work, pure urea and thiourea doped LAP crystals were grown by the slow evaporation method as reported by the earlier authors. The

grown crystals were subjected to various characterization measurements.

### Experiments

All the starting materials were of analytical reagent grade and used as purchased. LAP was prepared by mixing L-arginine with orthophosphoric acid in 1:1 mole ratio. The mixture was placed in a magnetic stirrer and stirred for about 3 hours. Long time stirring was done for the homogeneous mixing of the mixture. In the solution growth technique, selection of a solvent which is moderately soluble plays an important role. In the present study water was used as the solvent for synthesis of the compound and growth of LAP crystals. The synthesized salt of LAP was used for solubility test and crystal growth after repeated recrystallization. The recrystallized LAP was dissolved in 100 ml of water at  $40^\circ\text{C}$ . After the saturated solution of LAP was obtained, it was filtered using a filter paper after preheating. The solution was optimally covered using a plane thin plastic sheet and placed in a constant temperature bath for crystal growth. Crystals of LAP were grown from its saturated aqueous solution by the slow evaporation technique within 7 days. Transparent crystals with high optical-quality were selected from the harvested crystals for characterization studies. Doped crystals were obtained by adding the dopants to LAP solution in the required molar concentration. The dopant concentration used in this study was 0.01 M. The dopant (urea or thiourea) was mixed with the pure

Fig. 1. Photographs showing the grown pure and doped LAP crystals

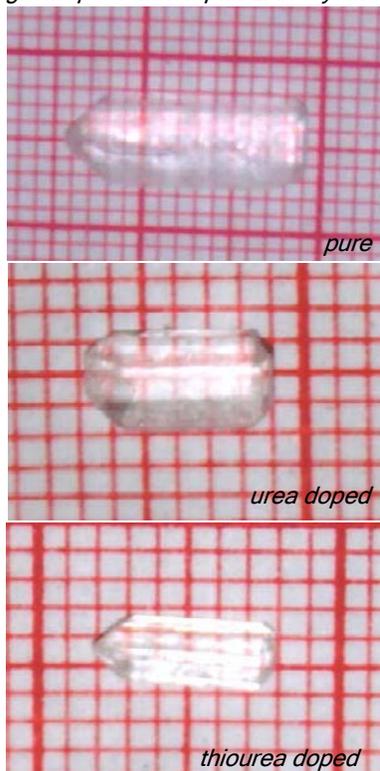


Fig. 2. FTIR spectrum of LAP crystal

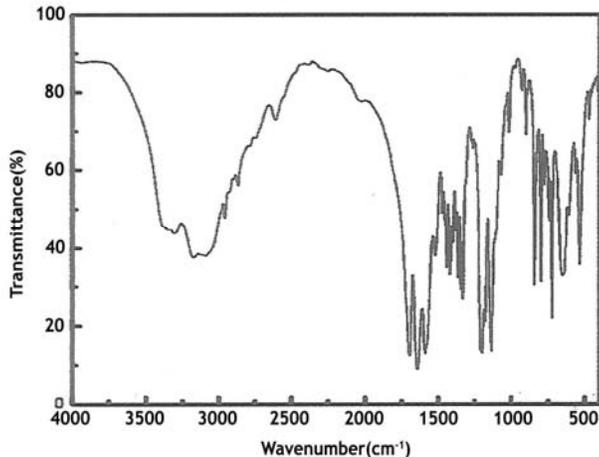


Fig. 3. FTIR spectrum of urea doped LAP crystal

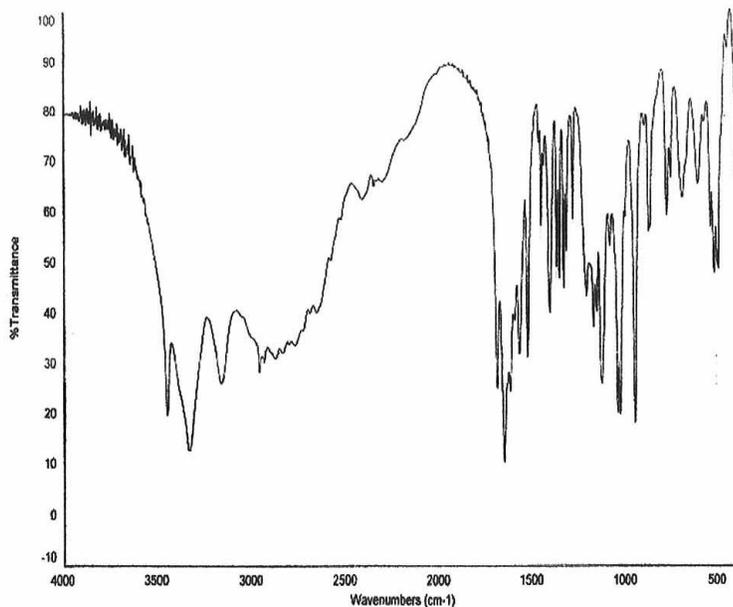


Fig. 4. FTIR spectrum of thiourea doped LAP crystal

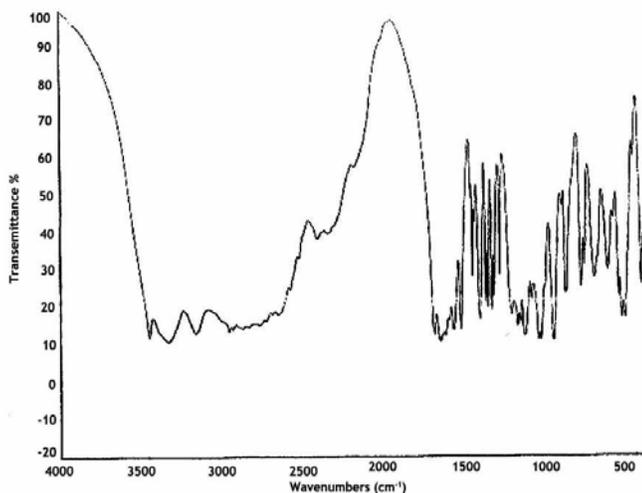


Fig. 5. TGA and DSC patterns of pure LAP crystal

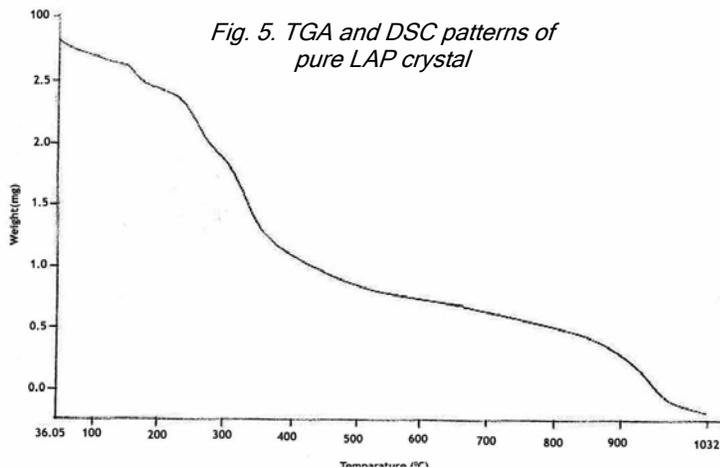


Table 1. Wavenumbers of absorption peaks and corresponding band assignment of the grown crystals

Wave numbers (in cm-1) of the absorption peaks			Band assignments
LAP	urea doped	thiourea doped	
3450	3449	3449	O - H or N - H stretching
3334	3332	3331	N - H stretching of the aliphatic secondary amine
3166	3165	3164	N - H stretch of the primary amine
2959	2961	2961	C = N-H stretching
1690	1690	1689	C = O stretching
1651	1651	1650	COO <sup>-</sup> amine
-	-	1371	C = S stretching

solution directly.

The vibrational measurements were carried out at room temperature. Fourier transform infrared spectra were obtained from potassium bromide pellets on a Thermo Nicolet, Avatar 370 FT-IR spectrometer in the region  $4000\text{-}400\text{cm}^{-1}$ . Thermo gravimetric analysis and differential scanning calorimetry analysis (TGA/DSC) were carried out in  $40\text{-}800^\circ\text{C}$  temperature range using a Perkin Elmer, Diamond TG/DTA instrument with a heating rate  $10^\circ\text{C}/\text{min}$  in nitrogen atmosphere. Samples were weighed in a platinum crucible with a microprocessor-driven temperature control unit and a data station. The SHG measurement was performed using the technique of Kurtz and Perry. An Nd: YAG laser with fundamental radiation of  $1064\text{ nm}$  was used as the optical source and directed onto the powder samples.

## Results and discussion

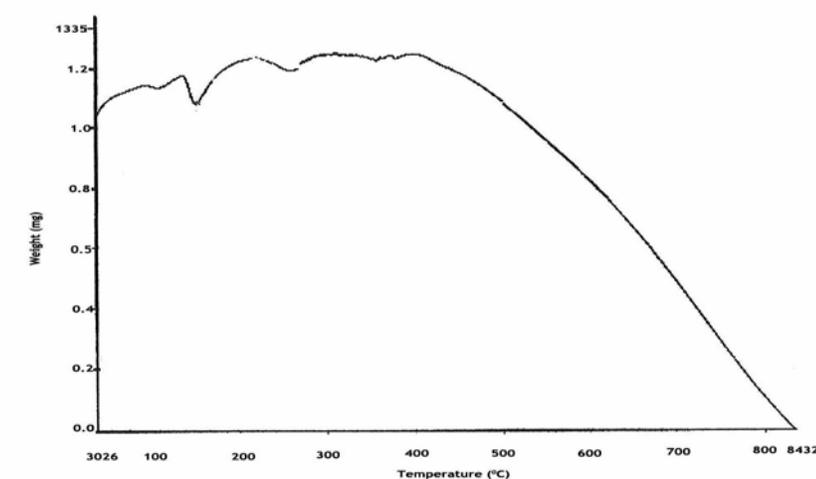
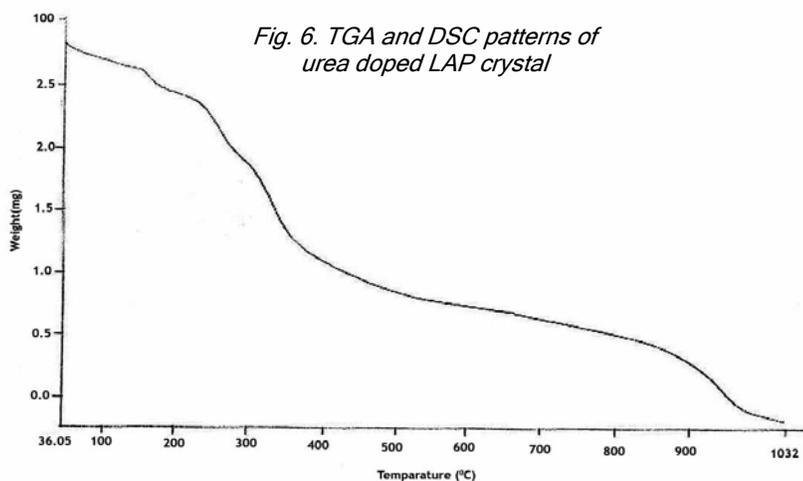
### Crystal growth

The doped crystals were found to be more transparent and perfect than the pure crystals. The morphological perfection of the doped crystals was better than the pure crystals grown in the present study. The maximum size of

the pure crystals obtained in the present study was  $11\text{ mm} \times 3\text{ mm} \times 3\text{ mm}$  and that of doped crystals was  $14\text{ mm} \times 4\text{ mm} \times 3\text{ mm}$ . The photographs of the grown crystals are shown in Fig. 1. It is observed that addition of urea or thiourea to LAP solution reduces the nucleation density and crystals grown were seen to have good morphological perfection than the pure crystal. The grown crystals were found to be non-hygroscopic and remain stable for more than 6 months, even after exposure to sunlight.

### FTIR studies

The FTIR spectra recorded for the grown crystals are presented in Fig. 2-4. The band assignments are presented in Table 1. The FTIR spectra and the corresponding band assignment clearly indicate that the functional groups of pure LAP are not altered by the addition of the dopants. Moreover the presence of absorption peak at  $1371\text{ cm}^{-1}$  confirms the presence of C=S stretching in the thiourea doped LAP crystal confirming that the dopant has entered into the LAP lattice which is absent in the pure and urea doped LAP crystals.



### Thermal studies

The TGA and DSC curves of LAP are shown in Fig. 5-7. From the TGA curve, one can see that the material starts decomposing above  $172^\circ\text{C}$ . This is supposed to be the utilization of the thermal energy in overcoming the valance bonding between the L-Arg+ cation and the phosphate anion, which happens during the initial stage of decomposition. Similar observation has been reported for L-arginine trifluoroacetate (Sun *et al.*, 2007). At this stage of decomposition the LAP crystals loses 2 molecules. At  $274^\circ\text{C}$ , the second decomposition starts with the evolution of carbon di-oxide. At  $350^\circ\text{C}$ , the third decomposition starts leaving the residue at the end of the heating process. Similar observations are noted for the doped crystals also. The decomposition of pure and doped LAP crystals are supported by the corresponding endothermic dips in the respective temperatures obtained in the DSC analysis. The expected stages of decomposition along with the % weight loss and expected loss of molecules are presented in Table 2.

### NLO studies

SHG may be employed as a tool to evaluate at least qualitatively the bulk homogeneity of the crystals under investigation. To check the nonlinear optical property of the grown crystal, Kurtz and Perry

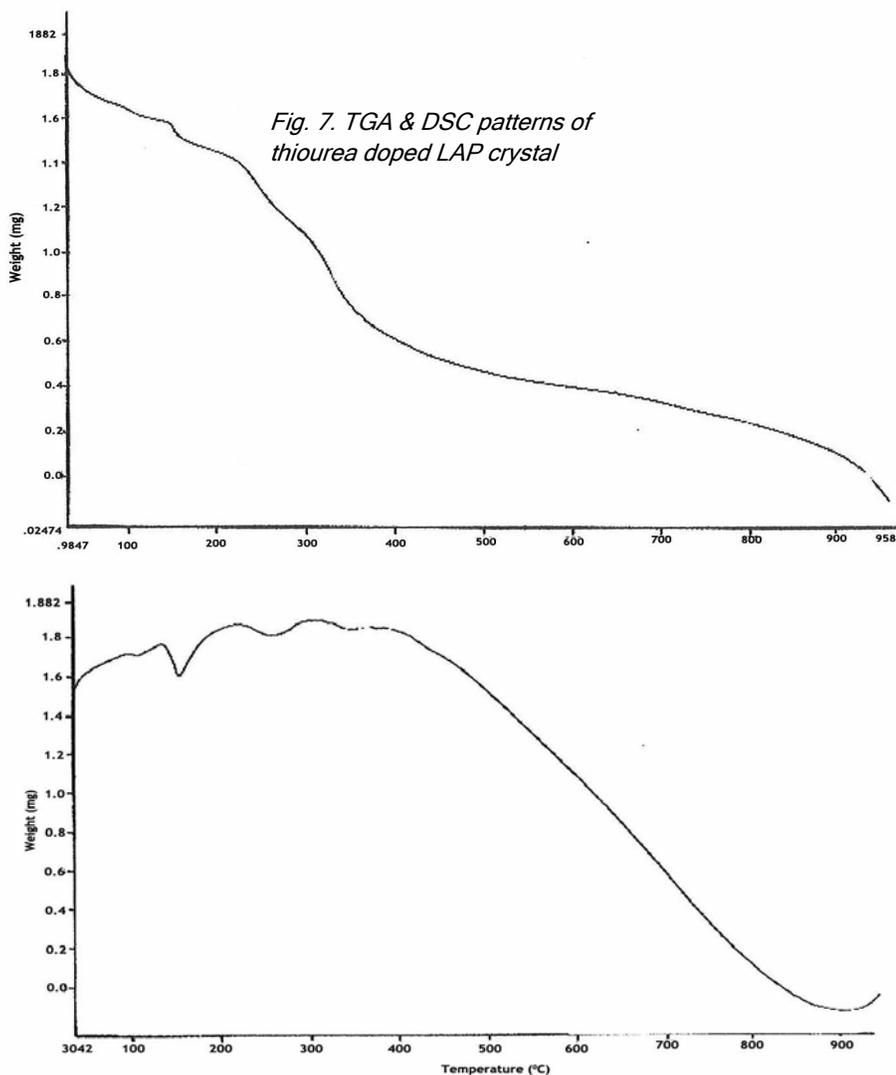


Fig. 7. TGA & DSC patterns of thiourea doped LAP crystal

technique was used (Kurtz & Perry, 1968). A high-intensity Nd: YAG laser with fundamental radiation of 1064 nm was used as the optical source and directed onto the powder sample of LAP. The SHG behaviour was confirmed from the output of intense green light emission ( $\lambda=532$  nm) from the crystal. Intensity of the bright green emission was estimated to be 2.5 times more than that of the standard KDP crystal.

### Conclusion

In this paper, the synthesis as well as single crystal growth of LAP has been reported. LAP crystals were grown by conventional low temperature solution growth method. FT-IR spectra confirm the various functional groups present in the grown crystal. The thermal studies on the grown crystals show that these crystals are thermally stable up to 172°C. The SHG intensity of LAP is found to be 2.5 times more than that of KDP, which shows that the crystal is a potential NLO material.

### References

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