



Growth of nonlinear optical material: *L*-arginine hydrochloride and its characterisation

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Abstract

L-arginine hydrochloride crystals have been grown using water and ethanol + water mixture as solvent. Growth of the anhydrous form of LAHCl has also been carried out. The grown crystals were subjected to powder X-ray diffraction studies. FTIR studies have been carried out to identify the functional groups present in the crystal. TGA and optical transmission studies have also been made on the grown crystals. The grown crystals were subjected to etching and microhardness studies.

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1. Introduction

Nonlinear optical (NLO) materials are attracting a great deal of attention because of their use in optical devices such as optical switches, optical modulators, electro-optical devices, etc. KDP group of materials remains the most widely used crystals for frequency conversion in spite of their modest nonlinearities [1]. This is primarily due to the low cost and the relative ease with which large

volumes of optically homogeneous material can be grown. Organic materials have been of particular interest because the NLO responses in this broad class of materials is microscopic in origin, offering an opportunity to use the theoretical modelling coupled with synthetic flexibility to design and produce novel NLO materials. However most organic NLO materials are susceptible to damage because of their poor mechanical and thermal properties [2]. Hence new type of NLO materials have been built from organic–inorganic complexes in which the high optical non-linearity of a purely organic compound is combined with the favorable mechanical and thermal properties of inorganic

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materials. An improved harmonic generator *L*-arginine phosphate monohydrate (LAP), one such semiorganic NLO material for laser fusion experiments to replace the conventional KDP crystals was discovered by Xu et al. [3]. LAP is three times more nonlinear than KDP, its damage threshold also two to three times higher than that of KDP, less deliquescent and more angularly sensitive compared to KDP [4,5]. LAP and its chemical analogues are formed from the strongly basic amino acid, *L*-arginine and various other acids. All the compounds in this class contain an optically active carbon atom, and therefore they form acentric crystals. Ten of these analogues of LAP were synthesised and their linear and NLO properties were studied specifically looking for phase matching that was less angularly sensitive than LAP or nonlinearities that were larger than LAP. The growth of other analogues of LAP like *L*-arginine hydrofluoride [6] has been reported. *L*-arginine hydrochloride monohydrate (LAHCl) is one of the new semiorganic NLO materials discovered by Monaco et al. [7]. Use of these crystals for NLO devices demands large size single crystals of extremely high quality. When *L*-arginine reacts with hydrochloric acid, it forms *L*-arginine chloride R^+Cl^- , which crystallises in hydrated and anhydrous forms: $C_6H_{15}N_4O_2Cl \cdot H_2O$ and $C_6H_{15}N_4O_2Cl$ [8]. Both the hydrous and anhydrous forms belong to the space group P_{21} with two molecules in the asymmetric unit and are optically biaxial. The intensity of the second harmonic generated from the powder sample (I/I_0) for the hydrated form of LAHCl is 2.4 and that for the anhydrous form is 1.5 relative to quartz [7]. Hence the present study aims for the growth and characterisation of the hydrated and anhydrous forms of the NLO material LAHCl.

2. Solubility studies

L-arginine hydrochloride (A.R) grade was taken and dissolved in triple distilled water. Solubility studies were carried out in a constant temperature bath with a cryostat facility. Stirring was achieved using an immersible magnetic stirrer. The solution

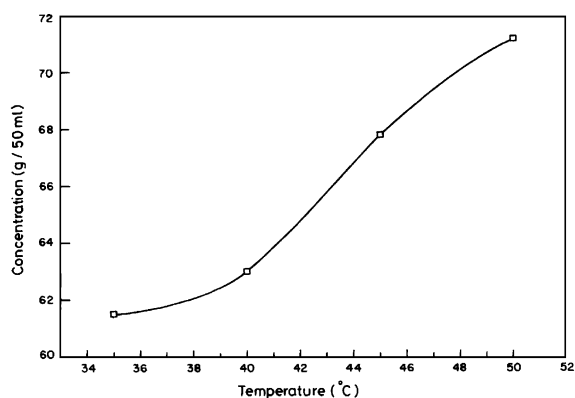


Fig. 1. Solubility of LAHCl in water.

was stirred continuously for 6 h. Solubility studies for different temperatures (35°C, 40°C, 45°C and 50°C) have been carried out. Solubility was determined by gravimetric analysis and the solubility curve of LAHCl is shown in Fig. 1. It has been found that the solubility of LAHCl was high in water. Hence a mixture of ethanol and water can be used for the growth to minimise the solubility of the solute in the solvent taken. Using the solubility the crystals were grown by slow evaporation and slow cooling technique.

3. Growth of LAHCl single crystals

The starting material *L*-arginine hydrochloride was dissolved in Millipore water of resistivity 18 MΩ cm in accordance with the solubility diagram. 500 ml of saturated solution of LAHCl at 45°C was prepared. Using a glass filter of 1 μ porosity, the solution was filtered using a peristaltic pump. Seeds obtained from slow evaporation technique which are defect free were selected for growth. The growth was carried out in a constant temperature bath of controlling accuracy $\pm 0.01^\circ\text{C}$. A cooling rate of 0.1–0.3°C/day was employed in the initial and final stages of the experiment. Once the room temperature is reached the crystal is harvested. A crystal of dimension $4.5 \times 4 \times 2 \text{ cm}^3$ has been grown and is shown in Fig. 2a. Fig. 2b shows the LAHCl single crystal grown using ethanol and water mixture (70% and 30%) as solvent.

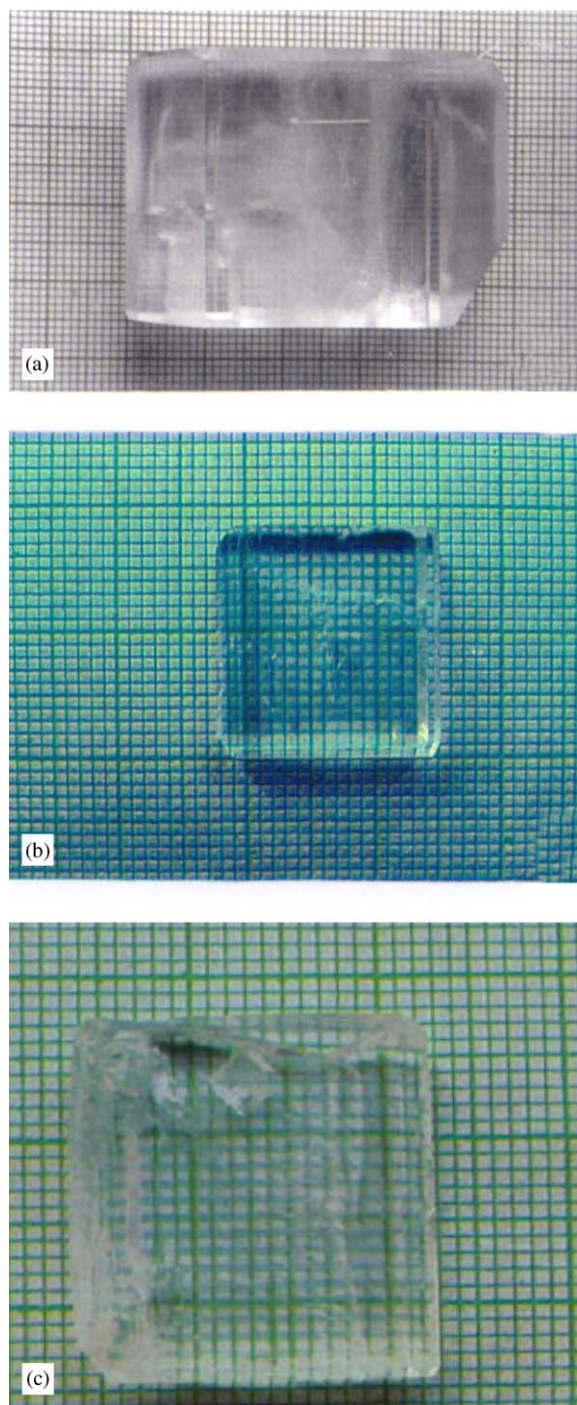


Fig. 2. As grown crystals of: (a) LAHCl using water as solvent, (b) LAHCl using ethanol+water mixture, and (c) LAHCl anhydrous.

The anhydrous form of *L*-arginine hydrochloride occurs at the growth temperature $t \geq 60^\circ\text{C}$. The solution was prepared according to the solubility data discussed above and the growth was carried out by slow evaporation technique at 60°C . The saturated solution was filtered with a glass filter of porosity 0.1μ and loaded in a beaker covered with a perforated lid. Crystals grown by slow evaporation technique are shown in Fig. 2c.

4. Crystal characterisation

4.1. Powder X-ray diffraction analysis

Powder X-ray diffraction pattern of the grown crystals were recorded using Rich Seifert Powder X-ray diffraction system. The lattice parameter values of *L*-arginine hydrochloride crystallised using ethanol and water mixture as solvent are $a = 11.314 \text{ \AA}$, $b = 8.298 \text{ \AA}$, $c = 11.054 \text{ \AA}$, $\beta = 91.044^\circ$ and $V = 1037.696 \text{ \AA}^3$ and that of anhydrous crystal are $a = 5.1937 \text{ \AA}$, $b = 9.487 \text{ \AA}$, $c = 20.0235 \text{ \AA}$, $\beta = 88^\circ 54'$ and $V = 986.3 \text{ \AA}^3$. They are found to be in good agreement with the reported values $a = 5.33 \text{ \AA}$, $b = 9.46 \text{ \AA}$, $c = 20.07 \text{ \AA}$, $\beta = 90^\circ 30'$ and $V = 1011.9 \text{ \AA}^3$ [7].

4.2. Single crystal X-ray diffraction analysis

The grown LAHCl crystal (using water as solvent) was analysed by the single crystal X-ray diffraction method. The data were collected at room temperature using SIEMENS AED single crystal X-ray diffractometer and $\text{MoK}\alpha$ radiation ($\lambda = 0.71069$) with a local system of programs. During the data collection time one standard reflection was monitored for every 100 reflections without significant variations. The experimental information and crystal data are summarised in Table 1.

4.3. Thermogravimetric analysis (TGA) of *L*-arginine hydrochloride monohydrate

The TGA analysis of LAHCl was carried out between 30°C and 600°C with a heating rate of $10^\circ\text{C}/\text{min}$. The thermogram and the differential

Table 1
Crystallographic information of LAHCl crystal grown using water as solvent

Formula	[C ₆ H ₁₅ N ₄ O ₂ · Cl · H ₂ O]
Formula weight	457.37
Crystal ; colour	Colourless
Crystal system	Monoclinic
Space group	P ₂₁
Cell constants <i>a</i> (Å)	11.044
<i>b</i> (Å)	8.483
<i>c</i> (Å)	11.208
Cell determination: θ range (deg)	1.82–30.06
Cell volume	1049.74
μ_{calc} (mm ⁻¹)	0.36
d_{calc} (gcm ⁻³)	1.447
Z	2
Temperature	293(2)
Diffractometer	SIEMENS AED
Radiation, Wavelength (Å)	MoK α , 0.71069
Standard reflection, step	One, every 100
Decay of standard	None
Reflections measured	5103
Reflections observed [$> 2\sigma(I)$]	4772
θ range(°)	
No. of refined parameters	390
R_1	0.0279
R_w	0.0699
GOF	1.016
Computer programs: solution	SIR 97
Refinement	SHELX 93 [12]

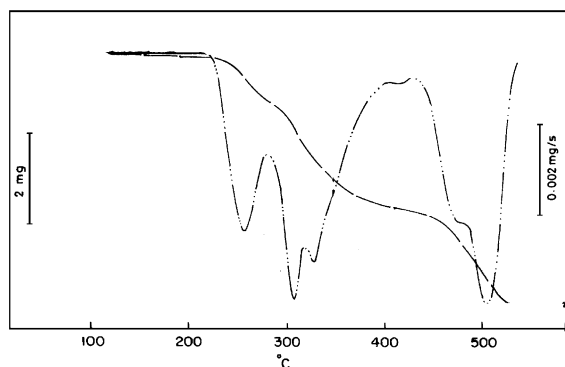


Fig. 3. TGA of LAHCl crystal grown using water as solvent.

thermogravimetric trace obtained are shown in Fig. 3. There are three stages of weight loss. The first weight loss starts at 100°C and ends at 140°C which is clearly assigned to loss of water. The total weight loss is found to be 9.09%. As the weight loss is sufficiently sharp, the released water is to be

from the crystal lattice. The second and third weight loss which is major in this analysis starts at 240°C and ends at 400°C. The total weight loss is found to be 81.54%. The decomposition leads to a residue of 18.45%. So the study clearly reveals the presence of lattice water.

The TGA of *L*-arginine hydrochloride crystallised from ethanol and water mixture bears the same characteristics as that of the previous one illustrating same stoichiometry of the crystal.

The TGA of LAHCl (anhydrous) was carried out between 40°C and 600°C. The heating rate employed was 10°C/min in air. The thermogram shows three major weight losses occurring at 220°C, 280°C and 420°C, but no weight loss is observed till the temperature reaches 220°C. So it can be suggested that the single crystal of LAHCl can be put into application upto 220°C without any observable loss of materials. In addition absence of physically adsorbed water or water of crystallisation is an interesting feature of the crystal obtained.

4.4. Fourier transform infrared analysis

The FTIR spectrum of LAHCl is shown in Fig. 4. There is a broad strong absorption between 3500 and 2000 cm⁻¹. It is due to the superimposed OH and NH₃⁺ stretching bands. Absorption in this region is characterised by multiple fine structures on the lower wave number side of the band. Presence of the OH stretch due to water could be

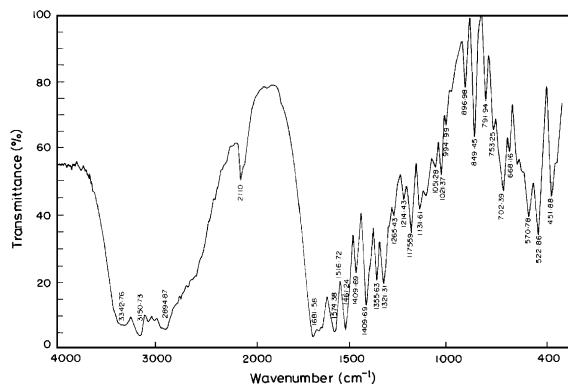


Fig. 4. FTIR spectra of LAHCl crystal grown using water as solvent.

conveniently assigned to the OH stretch at 3382.97 cm^{-1} and OH bend at 1627.65 cm^{-1} . The asymmetric and symmetric NH bends of NH_3^+ are seen at 1627.65 and 1500 cm^{-1} , respectively. Similarly the asymmetric and symmetric CO_2 stretching modes are observed at 1595.74 and 1400.70 cm^{-1} . The torsional oscillations of NH_3^+ can be assigned to the peak at 546.05 cm^{-1} . The C=O stretch is observed at 1666.26 cm^{-1} . The alkyl CH stretching mode is positioned at 2936.17 cm^{-1} and the corresponding CH_2 bend is placed at 1446.80 cm^{-1} . The characteristic peak due to C–C–O group produces an intense broad band between 1000 and 1200 cm^{-1} . The FTIR spectra of LAHCl using ethanol and water mixture shows broadening due to the presence of OH stretch and the peaks are well resolved compared to the crystal grown using water solvent.

FTIR analysis of the grown crystal (anhydrous LAHCl) was carried out using KBr pellet technique. The broad envelope between 3400 and 2200 cm^{-1} is due to the overlapping of peaks of the asymmetric stretching modes of NH_2 (3150.73 and 3342.76 cm^{-1}) and alkyl CH stretching mode (2894.87 cm^{-1}). In addition hydrogen bonding interaction between NH_3^+ group with the neighbouring molecules in the crystal lattice contributes much to the peak broadening. The presence of well-defined symmetrical and asymmetrical modes of NH_2 in this envelope evidently prove protonation of secondary amino grouping (NH) rather than NH_2 attached to azomethyne group. The peak broadening also reveals that the packing cores in the crystal lattice are largely due to dipolar and hydrogen bonding interaction. There is an overtone at 2110 cm^{-1} which may be assigned to a combination of 1175.89 and 1021.37 cm^{-1} . The intense peak at 1681.58 cm^{-1} is due to the C=O stretch of carboxylate ion. The C–N stretch and CH_2 bending modes are observed at 1574.38 and 1461.24 and 1355.8 cm^{-1} . The torsional oscillation of NH_3^+ group is observed at 522.86 cm^{-1} . The symmetric carboxylate C=O stretch is positioned at 1409.69 cm^{-1} . The peak at 702.39 cm^{-1} is assigned to C–H rocking vibration. The IR spectrum indicates the absence of water as there is no peak due to OH stretch at 3400 cm^{-1} .

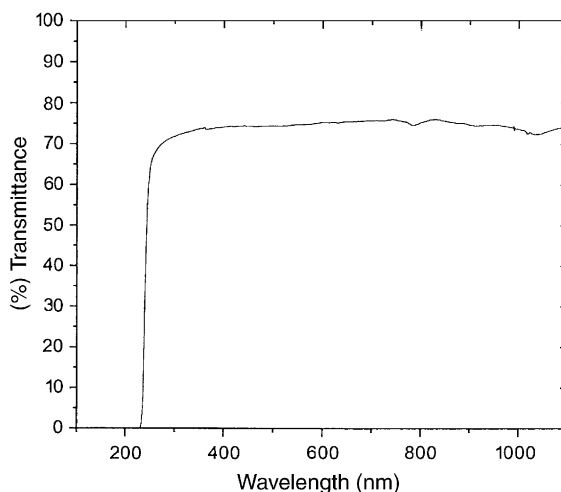


Fig. 5. Transmission spectra of LAHCl crystal grown using water as solvent.

4.5. Optical transmission studies

Optical transmission spectra have been recorded using Cary 17D spectrophotometer. The spectra were recorded in the wavelength 200 – 1100 nm . Fig. 5 shows the optical transmission spectra of LAHCl crystal crystallised using water as solvent. It is found that LAHCl crystallised using water solvent has a transmittance of 74% and that crystallised using ethanol and water mixture shows a transmittance of 69% . The lower UV cut-off for both the crystals are at 233 nm .

The UV–Visible light transmittance of the anhydrous form of LAHCl single crystal is examined between 200 and 1000 nm . The material is found to be transparent to all radiations in the wavelength range 300 – 1000 nm . Just above 300 nm , there is an absorption illustrated by a decrease in transmittance. This is due to $n \rightarrow \pi^*$ transition in azo methyne group. The steep decrease in transmittance around 250 nm may be assigned to electronic excitation in COO group. As there is no change in the transmittance in the entire visible range upto 300 nm , the materials can find application as window in spectral instruments in those regions.

4.6. Etching studies

Etching may be considered as a reversal of crystal growth and therefore, a surface step, for example, a screw dislocation will dissolve more easily than a flat surface layer [9]. In the present case, water as well as ethanol and water mixture (70% and 30%) have been used as etchants. The etching was carried out for 30 s in all the cases while stirring the etchant continuously. The etched samples were observed using Leitz Weitzlar optical microscope. Well-defined rectangular etch pits were observed in all cases for both the etchants on the (100) plane of the crystal. A similar morphology of rectangular etch pit was observed in *L*-arginine hydrobromide using alcohol and acid as etchants [10,11]

4.7. Microhardness studies

The polished surface of the (100) plane of the grown crystal was subjected to static indentations at room temperature in air using Leitz Weitzlar microhardness tester fitted with a Vickers diamond pyramidal indenter. Several trials of indentation were made on the (100) plane of the grown crystal for each load and the average value of the diagonal length of the indentation marks at each load was taken. Table 2 shows the Vickers micro-hardness values of LAHCl crystal and some known NLO materials.

4.8. NLO studies

A Q-switched Nd:YAG laser (1064 nm) was used and the powder SHG studies of LAHCl crystal were carried out by Kurtz Powder technique. Intense green light has been observed. KDP sample was used as the reference material and the output

power intensity of LAHCl was comparable with the output power of KDP. The intensity of green light is more in the case of hydrated LAHCl crystal than that of anhydrous LAHCl crystal. This result agrees with earlier report by Monaco et al. [7].

5. Conclusion

LAHCl single crystals have been grown using water as solvent by the slow cooling method. Solubility of LAHCl has been carried out for different temperatures. As the solution is highly viscous, ethanol and water mixture in the ratio 70:30, respectively, has been chosen as solvent and crystal growth by slow evaporation was carried out. The solubility of the solvent in the above solute is reduced considerably. The anhydrous form of LAHCl has also been crystallised at 60°C. Lattice parameter values were found using powder and single crystal X-ray diffraction analyses. TGA showed the presence and absence of water in the *L*-arginine hydrochloride monohydrate and *L*-arginine hydrochloride (anhydrous) crystals, respectively. Optical transmission studies show an increased percentage of transmittance for LAHCl using water as solvent. FTIR studies confirmed the various functional groups present in the crystals. Rectangular etch pits were observed in the (100) plane of the grown crystals. Hardness of LAHCl using ethanol and water mixture was found to be higher than that crystallised from water solvent.

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Table 2

Vickers hardness values of *L*-arginine hydrochloride crystals (A comparative data with some known *L*-arginine family crystals)

S. No	Sample name	Vickers hardness H_v (kg/mm ²)
1	<i>L</i> -arginine hydrochloride (water as solvent) (LAHCl)	178 (present study)
2	<i>L</i> -arginine hydrochloride (ethanol + water as solvent) (LAHCl)	190 (present study)
3	<i>L</i> -arginine hydrobromide (LAHBr)	47.98 [13]
4	<i>L</i> -arginine tetrafluorborate (LAFB)	62.5 [14]
5	LAHClBr	114.46 [15]

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