RESEARCH ARTICLE

Effect of Added Impurities on the Properties of LAHCL Single Crystals

M Meena1, C.K Mahadevan2, R Sukthi Sudar Saravan3, V. N Praveen4

1Department of Physics, S.T. Hindu College, Nagercoil-629 002, Tamilnadu, India.
2School of Basic Engineering and Sciences, PSN College of Engineering and Technology, Tirunelveli-627 152, Tamilnadu, India.
3Department of Physics, Chikkanna Government Arts College, Tiruppur-631 002, Tamilnadu, India.
4Department of Physics, Mahatma Gandhi College, Thiruvananthapuram, Kerala, India.

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ABSTRACT

L-arginine hydrochloride (LAHCl) is the material of interest in our study which has peculiar optical, nonlinear and dielectric properties. This study is carried out for knowing about the influence of organic and inorganic impurities on the physical and chemical properties of LAHCl single crystals. Slow cooling technique is employed to grow both pure and impure LAHCl crystals. The obtained crystals were then exposed to micro hardness, dielectric measurements and AC conductivity measurements. This aids in understanding the physical properties of the developed crystals. Kurtz and Perry second harmonic generation test was used to confirm the optical and non-linear properties of the grown crystals. It was found to be approximately 5 times that of potassium dihydrogen orthophosphate crystal. The outcomes and conclusive results are discussed in detail.

Key words: Slow cooling technique, X-ray diffraction, Non-linear optical material, Micro hardness, SHG efficiency, Organic compounds.

1. INTRODUCTION

Non-Linear Optical (NLO) organic materials and Second Harmonic Generation (SHG) test has a wide range of practical applications viz in the areas of optoelectronics [1], photonics [2], telecommunication [3], laser remote sensing, optical computing, laser driven fusion, optical storage and colour displays [4]. They also have a role to play in extending the available limited frequency from a laser source [5]. There are various non-linear phenomena in practice in the overall crystal arena. Frequency conversion is one such phenomenon which helps in extending the laser wavelength range, optical communications and optical image storage [6]. Numerous trials have been carried out for synthesizing, identifying, characterizing and developing a group of Non-Linear Optical (NLO) materials which can be used in frequency conversion applications [7]. The organic materials are of interest since the nonlinear optical responses are microscopic in origin. This gives a chance to explore theoretical modelling along with synthetic flexibility to plan and create advanced materials. Most of the organic NLO crystals possess negligible thermal and mechanical properties [8] and are vulnerable to damage while processing. Considering this, a new NLO material have been developed from organic-inorganic complexes. In this case the optical non-linearity is taken from organic compounds and the needed thermal and mechanical properties are taken from inorganic materials. An example of such a hybrid material is L-arginine hydrochloride (LAHCl) which is of interest in our study. Our objective was to recognize an extremely new material for photonic application. Hence we began with amending the LAHCl properties by doping it with KCl, NaCl, glycerine and urea at 0.5 mole %. The existence of different dopant molecules at considerably lower parent solute concentrations was observed. It also contributed to the growth kinetics. Numerous interesting and peculiar results are explained based on multiple properties of dopped KDP
In our investigation, slow cooling technique has been used to grow pure LAHCl, and glycine, KCl, NaCl and urea added LAHCl single crystals. The melting point and solubility points were assessed. The major characteristics of the grown crystals included mechanical and SHG efficiency, electrical studies and single crystal X-ray diffraction.

2. EXPERIMENTAL PROCEDURE

2.1. Synthesis of pure and doped LAHCL salt

L-arginine and hydrochloric acid of high purity are taken in equimolar ratio and from them the starting material was synthesized. An aqueous LAHCl solution was prepared by dissolving hydrochloric acid and equimolar amount of L-arginine in double distilled water. The reaction between L-arginine and hydrochloric acid resulted in the production of LAHCl salt and their corresponding chemical reaction is shown as follows.

\[(\text{NH}_2\text{O})\text{NHNCNH(CH}_2)_2\text{CH}(\text{NH}_2)\text{COOH} + \text{HCl} + \text{H}_2\text{O} \rightarrow (\text{NH}_2\text{O})\text{CNH(CH}_2)_2\text{CH}(\text{NH}_2)\text{Cl}\]

For preparing doped LAHCl crystals, NaCl, KCl, glycine and urea in a 0.5 mole percentage was separately added to pure LAHCl. The solvent is then made to evaporate. Now the synthesized pure and doped LAHCl single crystal was collected.

2.2. Solubility

The solvent should be selected in a careful manner as we require a moderately soluble solvent for usage in the slow cooling technique in order to develop bulk crystals from the solution. The developed crystal size depends on different factors such as the quantity of material present in the solution and the readiness of solubility in the solvent. So we have calculated NaCl, KCl, urea, glycine doped and pure LAHCl solubility in double distilled water. The pure and doped crystal solubility has been estimated using water as a solvent at various temperatures ranging from 30-45°C in containers which are air tight. The solubility of pure and doped LAHCl crystals which is temperature dependent is shown in figure 1. It is established that the solubility of NaCl, KCl, urea and glycine doped as well as pure LAHCl crystals rises with increase in temperature. Solubility is found to be reduced for glycine doped samples, KCl, NaCl and urea in comparison with pure LAHCl.

2.3. Growth of pure and doped LAHCL single crystals

The solubility data was employed to prepare pure and NaCl, KCl, urea and glycine doped LAHCl supersaturated solutions. The solution is stirred and filtered using quality filter papers. The pore size of such filter papers was around 1µm. The filtered solution was then allowed to slowly evaporate at a constant temperature of 27°C. Tiny crystals developed in the experimental vessels after an evaporation period of 5-7 days owing to spontaneous nucleation. Optical quality seed crystals which are transparent and macro defect-free were picked for growing bulk crystals. This is done by means of a crystal growth apparatus, by gradually varying the cooling rate from 60 °C to 45 °C of the aqueous saturated solution of both type of LAHCl. The seed crystal was attached to a clean silk thread and was gradually lowered into the solution. Good optical quality crystals of a noted dimension of 10x4x3 mm³ were grown in a 50-60 day period. Figure 2 displays the photograph of both pure and doped LAHCl single crystals obtained.

![Figure 1. Solubility diagram of pure LAHCl single crystals](image1)

![Figure 2. Photographs of (a) pure LAHCl (b) NaCl doped LAHCl (c) KCl doped LAHCl (d) urea doped and (e) glycine doped LAHCl single crystals](image2)

2.4. Characterization

The studies of grown crystals were carried out using ENRAF NONIUS CAD4
single crystal X-ray diffractometer with $M_{\text{K}}$ (λ = 0.717 Å) radiation. Kurtz and Perry powder technique (Kurtz and Perry 1968) was used to validate the NLO test of pure and doped LAHCl crystal. It was done using a Q-switched, mode locked Nd: YAG laser emitting 1.06 μm, 8 ns laser pulses with a spot radius of 1 mm. Leitz Wetzlar Vickers were used to carry out the micro hardness studies. It was facilitated by a micro hardness tester. The operation was carried out at room temperature. The tester was fitted with a Vickers diamond pyramidal indenter and an incident light microscope. The crystal plate is cut along the (0 0 1) direction at a thickness of 2 mm (± 0.15 mm). Then graphite was coated on the crystal plate surface. This was done to maintain a better electrical contact. The dielectric loss factor and the frequency dependent capacitance denoted as tan δ and C respectively were measured. These assessments were carried out on the prepared crystals with an accuracy of ± 1 %. The instrument used was Agilent 4284A LCR meter in the temperature range of 40 – 150 °C. The readings were recorded during the sample cooling process. It was done using the sample conventional two-probe technique [17]. Temperature was kept at a level of ± 1 °C. The crystal dielectric constant ($\varepsilon_r$) was calculated by the following relation in (2.1),

$$\varepsilon_r = \frac{A_{\text{air}}}{A_{\text{cryst}}} \left( C_{\text{cryst}} - C_{\text{air}} \right) \frac{1 - A_{\text{cryst}}}{A_{\text{air}}}$$

(2.1)

where

$C_{\text{cryst}}$ = Capacitance of the crystal  
$C_{\text{air}}$ = Capacitance of air  
$A_{\text{cryst}}$ = Area of crystal touching the electrode  
$A_{\text{air}}$ = area of electrode.

The AC electrical conductivity ($\sigma_{ac}$) was calculated using the equality in (2.2),

$$\sigma_{ac} = \varepsilon_0 \varepsilon_r \omega \tan \delta$$

(2.2)

where

$\varepsilon_0$ = Permittivity of free space (8.854 x 10^{-12} F/m)  
$\omega$ = Angular frequency ($\omega = 2\pi f$; f = 1 kHz for the present study).

The main aim of the single crystal X-ray diffraction technique was to find the lattice parameters of pure and doped LAHCl crystals. MoKα (λ=0.717 Å) radiation have been used to collect data at room temperature. It was evident that almost all the crystals have a monoclinic structure. P2₁ was the identified space group. The pure LAHCl single crystal data was found to be in good rapport with the forwarded values. It point towards the fact that the developed crystal is L-arginine hydrogen chloride (LAHCl) [18]. Table 1 displays the observed cell volumes and lattice parameters. Small disparities have been noted in the NaCl, KCl, urea and glycine doped LAHCl single crystal in terms of lattice parameters. In addition to it the NaCl, KCl, urea and glycine dosage in pure LAHCl crystal results in contraction of the corresponding unit cell volume.

3.2. Nonlinear optical studies

Pure and doped LAHCl crystals have been subjected to various processes for the preparation of powder samples. These samples were then subjected to nonlinear tests and the energy efficiency was confirmed by the green light emission of the powder sample. For the calculation of SHG efficiency, microcrystalline material of the sample KDP has been used as the reference. When a laser input with a power intensity of 10.8 mJ was made to pass through pure LAHCl and NaCl, KCl, urea and glycine doped LAHCl, second harmonic signals of 275 mV, 281 mV, 288 mV, 300 mV and 291 mV respectively were obtained as the output power intensity. The SHG efficiency of pure and NaCl, KCl, urea and glycine doped LAHCl is nearly about 5 times that of the reference material of the KDP crystals (53 mV). The addition of dopants into the LAHCl crystal increases its SHG efficiency.

3.3. Micro hardness studies

Device fabrication greatly depends on the mechanical strength of the materials. The deciding factor in choosing the processing steps of bulk crystals in device fabrication is Vicker’s hardness. The study was conducted and the indentations were made on the (0 0 1) plane of both type of LAHCl crystals. The indentation time was kept constant at 15 seconds. The load was varied from 5 to 25 grams. $H_v$ denotes the Vicker’s micro hardness.
number and was estimated by the following equation shown in (3.1),
\[ H_v = 1.8544 \left( \frac{P}{d^2} \right) \]  
(3.1)
where \( P \) = indenter load (g) and \( d \) = the diagonal length of the impression in μm

The mean of the obtained impressions were obtained and was regarded as the micro hardness value. The variations among Vicker’s values on the pure as well as doped LAHCl crystals with load are depicted in figure 3. The figure clearly explains that with the increase in load the hardness number decreases. This indicates a normal Indentation Size Effect (ISE) [19]. The load and diagonal length can be related by Meyer’s law [20] which can be written as follows in (3.2)
\[ P = Ad^n \]  
(3.2)
where \( A \) = Material’s constant and \( N \) = Meyer’s index

The work hardening coefficients are found to be 1.77, 1.5, 1.79, 1.75 and 1.77 respectively for pure LAHCl and NaCl, KCl, urea and glycine doped LAHCl respectively. The study conducted by [21] and [22] says that for hard materials \( n \) should be between 1 and 1.6 and above 1.6 for soft materials. On considering this, the pure LAHCl and KCl, urea and glycine doped LAHCl crystals can be categorized under soft materials. On the other hand NaCl doped LAHCl crystals comes under hard materials.

![Figure 3](image3.png)
Figure 3. Microhardness values versus load for pure and doped LAHCl crystals

3.4. Electrical studies

Figure 4.(a-c) shows the variation of dielectric loss factor (\( \tan \delta \)), dielectric constant (\( \varepsilon_r \)) and AC electrical conductivity (\( \sigma_{ac} \)) for pure and doped LAHCl crystals at 1 kHz frequency as a function of temperature along (0 0 1) direction. The small value of dielectric loss shows that the grown crystals are of higher quality possessing fewer defects.

A high dielectric constant is observed at 1 kHz frequency. This is due to the existence of different types of polarizations [23]. One of such polarizations namely space charge polarization is heavily dependent on the sample purity. Dielectric constant and dielectric loss has very large values and they may be credited to the above mentioned polarization owing to charged lattice defects [24]. The dielectric measurements tell us that silica replacement [25] in microelectronics industry may be probable with the usage of LAHCl crystals because of its lesser \( \varepsilon_r \) values.

![Figure 4](image4.png)
Figure 4. Variation of (a) dielectric constants (b) dielectric loss factors (c) AC electrical conductivities for pure and doped LAHCl single crystal.

4. CONCLUSION
Slow cooling technique was used to develop single crystals of pure and NaCl, KCl, urea and glycine doped LAHCl which are of higher quality. Aqueous solutions were used to assess the solubility. The crystal lattice parameters were in close agreement with the reported values. The SHG test authorizes the conversion efficiency of the crystal. It is found to be approximately 5 times greater than that of KDP crystal. Micro hardness studies were done to study the mechanical behaviour of both type of LAHCl crystals. Dielectric measurements revealed that the dielectric constant and ac electrical conductivities of pure as well as doped LAHCl rises with increasing temperature. The addition of impurity in the LAHCl crystal leads to a reduction of dielectric constant for a wide temperature range.

REFERENCES


[22] M.Hanneman, Metall, Manch, 1941.


### APPENDIX A

Table A1. Lattice parameters of pure and impurity added LAHCl crystal from single crystal X-ray diffraction

<table>
<thead>
<tr>
<th>Lattice parameters</th>
<th>Pure LAHCl</th>
<th>LAHCl-NaCl</th>
<th>LAHCl-KCl</th>
<th>LAHCl-Urea</th>
<th>LAHCl-Glycine</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>5.331</td>
<td>5.371</td>
<td>5.304</td>
<td>5.356</td>
<td>5.278</td>
</tr>
<tr>
<td>b (Å)</td>
<td>9.460</td>
<td>9.41</td>
<td>9.5</td>
<td>9.39</td>
<td>9.37</td>
</tr>
<tr>
<td>c (Å)</td>
<td>20.07</td>
<td>20.2</td>
<td>19.98</td>
<td>19.86</td>
<td>20.15</td>
</tr>
<tr>
<td>α°</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β°</td>
<td>90°30’</td>
<td>90.3</td>
<td>90.65</td>
<td>90.21</td>
<td>90.71</td>
</tr>
<tr>
<td>γ°</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>Crystal System</td>
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<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
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<td>P2₁</td>
<td>P2₁</td>
<td>P2₁</td>
<td>P2₁</td>
</tr>
<tr>
<td>Volume (Å³)</td>
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<td>1020.92</td>
<td>1006.696</td>
<td>998.812</td>
<td>996.448</td>
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