Growth and thermal studies of non-linear optical L-argininium diiodate
L-argininium dinitrate and L-argininium hydrochloride bromide single crystals

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Single crystals of L-argininium diiodate (LADI), L-argininium dinitrate (LADN) and L-argininium hydrochloride bromide (LAHClBr) were grown by slow solvent evaporation technique at room temperature. The grown crystals were characterized by X-ray diffraction, Differential Thermal Analysis (DTA), Thermogravimetric analysis (TGA) and Differential Scanning calorimetry (DSC). LADI crystallizes in the orthorhombic system, with space group $P2_12_12_1$. The XRD data prove that both LADN and LAHClBr crystals are monoclinic in structure with $P2_1$ space group. LADN is found to be thermally more stable than LADI and LAHClBr crystals.

Keywords: Growth from solution, Analogs of LAP, Non-linear optical, Differential scanning calorimetry, Microhardness
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1 Introduction
Non-Linear optical (NLO) materials play an important role in the field of fiber optic communication and optical signal processing. Complexes of amino acids with inorganic salts are promising materials for optical second harmonic generation (SHG) as they tend to combine the advantages of the organic amino acid with that of the inorganic salts. L-arginine phosphate monohydrate is a novel semi organic non-linear optical material whose structure was solved by Aoki et al. Many researchers carried out a wide search for new compounds and crystal of LAP analogs. Petrosyans et al. reported a new class of arginine compounds with composition Arg. 2 Ax (where Ax is an inorganic or organic acid).

In the present paper, the growth and characterization of L-argininium diiodate (LADI), L-argininium dinitrate (LADN) and L-argininium hydrochloride bromide (LAHClBr) crystals have been studied. From structural point of view, LADI crystallizes in the orthorhombic system, whose lattice parameters are $a = 6.9554\,\text{Å}$, $b = 7.998\,\text{Å}$ and $c = 25.038\,\text{Å}$, $\alpha = \beta = \gamma = 90^\circ$ with space group $P2_12_12_1$.

The NQR and IR studies indicate that the formation of Arg.2HIO$_3$ is a peculiarity of the arginine structure (namely, due to the existence of both amino and guanidyl groups) and not the property of HIO$_3$ to form acid compounds. L-Arg.2HNO$_3$ (LADN) can be crystallized from solutions containing Arg.HNO$_3$ in ratios from 2 to 10. L-Arg 2HNO$_3$ crystallizes in the monoclinic system whose lattice parameters are $a = 7.754\,\text{Å}$; $b = 7.286\,\text{Å}$; $c = 11.673\,\text{Å}$; $\alpha = 90^\circ$; $\beta = 92.6^\circ$ with space group of $P2_1$.

LAHClBr crystallizes in monoclinic system with space group $P2_1$, and the lattice parameters are $a=11.158(2)\,\text{Å}$, $b=8.579(3)\,\text{Å}$, $c=11.235(3)\,\text{Å}$ and $\beta=91.55(4)^\circ$. Surface micromorphology and growth mechanism of LAHClBr have been recently studied using Chemical etching technique by Pal et al. In the present paper, we report the growth and thermal studies of LADI, LADN and LAHClBr crystals.

2 Experimental Details
Stoichiometric amount of high purity L-arginine (Merck 99%) and iodic acid with double distilled water were used to prepare the solution of LADI. Seed crystals were formed due to spontaneous nucleation. Transparent good quality seed crystals were used for growth experiments. Good optical

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quality crystal up to a dimension of $14 \times 6.5 \times 5 \, \text{mm}^3$ was obtained in a period of 45-50 days. Figure 1(a) shows the photograph of as grown crystal of LADI, grown by slow evaporation technique at room temperature.

High purity L-arginine (Merck 99%) and nitric acid in the ratio 1:4 with double distilled water were used to prepare the solution of LADN. Seed crystals were formed due to spontaneous nucleation. Transparent good quality seed crystals were used for growth experiment. Crystals up to a dimension of $29 \times 8 \times 1 \, \text{mm}^3$ were obtained in a period of 30 days by slow solvent evaporation technique, at room temperature. Fig. 1(b) shows the photograph of as grown crystals of LADN.

LAHClBr was synthesized by dissolving one mole of L-arginine (Merck 99%) in double distilled water containing one mole of HCl and one mole of HBr acid. Single crystals of dimension $12 \times 9 \times 7 \, \text{mm}^3$ were obtained in a period of 50 days. The photograph of as grown crystals of LAHClBr is shown in Fig. 1(c).

The single crystal X-ray diffraction studies of the crystals were carried out using ENRAF NONIUS CAD4 single X-ray diffractometer with MoK$_\alpha$ ($\lambda = 0.717 \, \text{Å}$) radiation. The structure was solved by the direct method and refined by the full matrix least-square technique using the SHELXL program. TGA, DTA and DSC studies of the crystals were carried out using the instrument NETZSCH STA 409C.

### 3 Results and Discussion

The single crystal XRD data of the crystals is given in Table 1. It is evident from the studies that LADI crystallizes in the orthorhombic, and both, LADN and LAHClBr in monoclinic system. The results are in good agreement with the reported work.$^{8,12}$

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<thead>
<tr>
<th>Table 1—Crystal data of LADI, LADN and LAHClBr crystals</th>
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<tr>
<td>LADN</td>
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<td>Crystal system</td>
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<td>$a$, Å</td>
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<td>Volume, Å$^3$</td>
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<td>Z</td>
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<td>Space group</td>
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The TGA analysis of L-arginine diiodate was carried out between 20$^\circ$-700$^\circ$ C at a heating rate of 10$^\circ$ C/min with nitrogen atmosphere. The thermogram of LADI crystal is shown in Figure 2. There is a sharp weight loss at 145$^\circ$C, which corresponds to about 93.98% of the sample and no other loss is observed further, this confirms the decomposition of the sample at 145$^\circ$C. The DTA analysis of LADI was carried out between 28-700$^\circ$C at a heating rate of 10$^\circ$C/min with
nitrogen atmosphere. The DTA trace is shown in Figure 3. There is a sharp exothermic peak at 147.4°C which coincides with the decomposition as shown in the TGA trace. The DSC analysis was done between 20°C and 170°C at a heating rate of 5°C min⁻¹ in nitrogen atmosphere. The DSC trace is shown in the Figure 4. There is a sharp endotherm close to 90°C, which can be assigned to melting of the sample since there is no corresponding weight loss in the TGA trace (Figure 2).

The thermogravimetric analysis of LADN was carried out between 28°C-1200°C at a heating rate of 10°C/min. The experiment was performed in nitrogen atmosphere. The resulting thermogram is shown in Figure 5. Although the TGA trace appears nearly straight up to 170°C, a careful examination of DTA thermogram reveals a minor peak around 100°C, which could be due to physically adsorbed water. But at 171°C, a steady decrease in weight loss is observed (17.54%) due to decomposition of the sample. There are also two more weight losses for the residue between 200°-350°C and the weight loss is equal to 50.53%. At higher temperatures above 400°C, the final stage of decomposition occurs giving a total loss equal to 30.65%.

The DTA of LADN was carried out between 28°-1200°C in nitrogen atmosphere at a heating rate of 10°C / min. The resulting DTA trace is shown in Figure 6. There is a weak endotherm starting at about 130°C, which may be assigned to isomorphic transformation, as there is no corresponding weight loss in the TGA trace. This is accompanied by a sharp endotherm at about 152°C due to its melting. Terzyan et al.¹² reported the melting point of LADN as 130°C but the melting point of the crystal was actually found...
to be 152°C in the present study. The result was also verified by us using the melting point apparatus. This is very much evident by a sharp endotherm starting at about 152°C due to its melting. This endothermic transition is followed by an intense sharp exotherm. It is matching with the intense weight loss in TGA starting at 171.6°C. There are two more endotherms between 200°-350°C due to the decomposition of the residue in two stages. Hence, the crystal can retain its texture up to 152°C. Since the compound undergoes isomorphic transformation at 130°C its application is restricted up to 130°C.

The DSC analysis was done between 20°-170°C at a heating rate of 5°C min⁻¹ in the nitrogen atmosphere and is shown in Figure 7. There is a minute broad endotherm between 117.7 and 133.5°C which matches with the isomorphic transformation mentioned in the DTA trace. This is followed by an intense endotherm at 154.4°C which is assigned for the melting of the sample. The melting point was separately determined using melting point apparatus and the value was verified for the salt. In the TGA, the decomposition was shown to occur close to 175°C. Based on this result, it can be said that the decomposition follows immediately after melting.

The TGA of LAHClBr was carried out between 28°-1200°C in the nitrogen atmosphere at a heating rate of 10°C / min. The resulting DTA trace is shown in Figure 8. There is a sharp weight loss with the maximum at about 124.3°C which is due to loss of water of crystallization. The total weight loss for this stage is equal to 6.63% which corresponds to loss of one water molecule. So the formula can be written as LAHClBr. H2O. This weight loss is followed by a major weight loss pattern between 230 and 420°C occurring in three stages. It is assigned to decomposition of the salt.

The DTA of LAHClBr was carried out between 28°-1200°C at a heating rate of 10°C / min in nitrogen atmosphere. The resulting thermogram is shown in Figure 9. There is a sharp endotherm with a maximum at 129.9°C. It coincides with the first stage of weight loss in the TGA trace. There is one more sharp endotherm at 209.8°C. But for this endotherm there is no corresponding weight loss in the TGA trace. Hence, this endotherm is assigned to melting of the compound. The melting point 208°C, was also reported by Pal et al. The subsequent endotherms that follow this melting corresponds to the decomposition of the compound in three different stages as illustrated in TGA.

The DSC analysis was done between 20°-130°C at a heating rate of 5°C min⁻¹ in nitrogen atmosphere and the DSC trace is shown in the Figure 10. There is a sharp endotherm starting at 98°C. This corresponds to the loss of water of crystallization in the lattice as mentioned in the TGA. This observation, therefore, suggests that the crystal can be used for NLO applications up to 98°C.
4 Conclusion

Single crystal XRD analysis confirmed that LADI crystallizes in orthorhombic system with P2₁2₁2₁ space group and both, LADN and LAHClBr crystallize in monoclinic system with space group P2₁. The thermal stability of the crystals decreases in the order LADN > LAHClBr > LADI.

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References