Growth and Thermal Studies of Doped and Pure Crystals of L-Argininium Dinitrate

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Abstract Single crystals of pure and Cu$^{2+}$ doped semiorganic L-argininium dinitrate (LADN) crystals were grown by slow solvent evaporation technique, with the vision to improve the physicochemical properties of the sample. Single crystal XRD studies of both pure and doped samples were carried out. The thermal (DTA, TGA and DSC) studies were carried out and the results are compared.

1. Introduction
Within the last few years, a great deal of research work has been carried out in non-linear optical materials. Both the inorganic and organic materials were investigated and it was found that the inorganic crystals were characterized by good stability and high transparency range but their second order coefficients were limited. In contrast organic crystals exhibited higher second order nonlinear coefficients but their transparency domain was reduced [1]. This triggered the search for inorganic-organic hybrid crystals. Complexes of amino acids with inorganic salts proved to be one such material with interesting non linear properties. The salt of amino acid like L-arginine phosphate monohydrate (LAP) is a more recent nonlinear optical material that has been proposed as a replacement for Potassium dihydrogen phosphate (KDP) crystal [2-4]. The structure of LAP was solved by Aoki et al [5]. In view of its encouraging non linear properties scientists tried to grow other salts of L-arginine [6-9].

L-arg.HNO$_3$ was one among the compounds described by Monaco et al, which precipitated as a fine non-crystalline powder [6]. Interestingly, Petrosyan et al was successful in crystallizing L-arg.2HNO$_3$ (LADN) from solution containing Arg:HNO$_3$ in ratios from 2 to 10 [9]. Ramasamy et al have determined the structure of L-argininium dinitrate (space group P2$_1$) and reported that the diprotonated argininium molecule is linked by a strong hydrogen bond to the nitrate anion [10]. Recently, Terzyan et al have also solved the structure of 2(L-arg.HNO$_3$).H$_2$O and L-arg.2HNO$_3$ [11].

Recent experiments reveal that nonlinear performance can be improved by bringing out the compositional modification and metallic substitutions [12-13]. Hence attempts have been made in the present study to investigate the NLO and thermal properties of LADN crystals with Cu$^{2+}$ metallic dopant. The authors have already reported the growth and characterization of L-argininium dinitrate (LADN) crystals [14].

2. Experimental
1.1 Crystal growth
Approximate amount of high-purity L-arginine (Merck 99%) and nitric acid with water were used to prepare the solution of LADN [14]. The following is the reaction

\[(\text{NH}_2)\text{NH}-\text{CH}(\text{CH}_2)_3\text{CH}-(\text{NH}_2)\text{COOH} + 4\text{HNO}_3 \rightarrow (\text{H}_3\text{N})^+\text{CNH}(\text{CH}_2)_3\text{CH}(\text{NH}_3)^+\text{COOH} (\text{NO}_3)^-2 + 2\text{HNO}_3\]

The product was purified by repeated re-crystallization typically thrice from double distilled water. The 100 ml saturated solution was kept in a beaker covered with perforated polyethylene lid at room temperature. The crystals were grown by slow solvent evaporation method. The rate of evaporation of the solution was found to be approximately 2 ml per day. In a period of 15 days, seed crystals of LADN were formed due to spontaneous nucleation. Optically clear, defect free crystals with perfect morphological face were chosen for further growth experiment. The pH of the solution was
maintained at 2.2. Cu$^{2+}$ Doped LADN crystals were also grown by adopting the same procedure. The concentration of Cu in the doped crystals was maintained as 0.2M. Single crystals of pure and Cu$^{2+}$ doped LADN are grown with dimensions upto 18 x 6 x 2 mm$^3$ and 52 x 13 x 3 mm$^3$ in a period of 45 days. Photographs of pure and doped LADN single crystals are shown in Figure 1 and 2.

The morphology of LADN crystal has been studied and reported by the author [14] and it is seen that both pure and doped crystals have increased elongation along the crystallographic b- axis.

2.2 Characterization

The X-ray data were collected using an automatic X-ray diffractometer (MESSRS ENRAF NONIUS, The Netherlands) with MoKα (0.717Å) radiation. The structure was solved by the direct method and refined by the full matrix least squares technique using the SHELXL program. The NLO efficiency of pure and doped LADN crystals was evaluated by Kurtz & Perry powder technique using a Q- switched mode locked Nd:YAG laser emitting 1.06nm, 6 ns pulses with spot radius of 1mm [15]. TG / DTA of the crystals were carried out using the instrument NETZSCH STA 409C. DSC analysis of the pure and doped crystals of LADN was carried out using the instrument NETZSCH DSC 204. The TG / DTA of pure and doped LADN was carried out between 28 – 1200°C at a heating rate of 10°C /min. The experiment was performed in nitrogen atmosphere. The DSC analysis was done in the range 20 - 120 °C for pure LADN and up to 200°C for doped crystals.

3. Results and Discussion

3.1 X-ray diffraction analysis

The unit cell parameter of pure and Cu$^{2+}$ doped crystals of LADN is presented in Table 1. It is observed from the table that both pure and doped LADN crystals belong to monoclinic system and $P2_1$ space group. The lattice parameters of pure LADN are in good agreement with the reported values [10,11,14].

3.2 NLO Studies

Kurtz SHG test was performed on pure and Cu$^{2+}$ doped crystals of LADN to confirm the second harmonic signal generation efficiency. For a laser input of 6.2 mJ, the second harmonic signal (532 nm) of 91.66, 184.74  and 201.65 mV were obtained through KDP , pure and Cu$^{2+}$ doped LADN samples respectively. This shows that the NLO efficiency of pure LADN crystal have been improved with metallic substitution.

3.3 Thermal Analysis

The TG- DTG traces for pure and Cu$^{2+}$ doped LADN is shown in Figures 3 and 4 respectively. The thermograms of pure and doped LADN crystals nearly appear similar with four stages of decompositions. The first stage of decomposition occurs at nearly 171°C which is increased to 178°C.
for Cu$^{2+}$ doped LADN. It is followed by two more weight losses between 200 and 350°C. At higher temperatures about 400°C the final stage of decomposition takes place resulting in the total loss of the residue.

### Table 1. Unit cell parameters of pure and Cu$^{2+}$ doped LADN single crystals

| Crystal System | Pure LADN | Cu$^{2+}$ LADN |
|----------------|-----------|-----------------|
| Crystal System | Monoclinic | Monoclinic |
| a (Å)          | 7.7532    | 7.75           |
| b (Å)          | 7.2779    | 7.28           |
| c (Å)          | 11.6754   | 11.68          |
| α°             | 90        | 90             |
| β°             | 92.7      | 92.56          |
| γ°             | 90        | 90             |
| Volume (Å$^3$) | 658.02    | 659            |
| Z              | 2         | 2              |
| Space group    | P2$_1$    | P2$_1$         |

The DTA of pure and doped LADN is shown in Figures 5 and 6 respectively. There is a weak endotherm observed around 145°C in both pure and doped LADN crystals. This corresponds to isomorphic transformation as there is no corresponding weight loss in TGA trace. The melting point of both the pure and doped LADN crystals was found to be nearly equal to 152°C. The melting of the sample is followed by a sharp exotherm starting around 171°C for pure LADN and at 178.2°C for doped sample.
The DSC trace for both pure and Cu$^{2+}$ doped LADN is shown in Figures 7 and 8. The minute endotherm corresponding to isomorphic transformation as mentioned in the DTA trace is seen in the DSC trace. It is seen from the trace that addition of dopants have enhanced the peak value to 142.7°C. This is followed by the endotherm assigned for the melting of the sample. DSC trace shows that decomposition follows immediately after melting. The decomposition temperature for doped LADN sample is enhanced to 185.9°C.

4. Conclusion
Single crystals of pure and Cu$^{2+}$ doped LADN were grown from aqueous solutions by slow evaporation technique at room temperature. The pH of the solution was maintained at 2.2. The grown crystals were characterized by XRD and Thermal studies. The NLO studies show that doping has improved the NLO efficiency of pure LADN crystals. From thermal studies it is observed that the presence of metal dopant (Cu$^{2+}$) increases the decomposition temperature of LADN.

5. References
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