Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Crystal Growth 277 (2005) 303–307
JOURNAL OF CRYSTAL GROWTH
www.elsevier.com/locate/jcrysgro

Growth and characterization of L-argininium dinitrate

Preema C. Thomas, Jolly Thomas, J. Packiam Julius, J. Madhavan, S. Selvakumar, P. Sagayaraj*

Department of Physics, Loyola College, Chennai 600 034, India.

Received 7 October 2004; accepted 4 January 2005
Available online 2 March 2005
Communicated by R.S. Feigelson

Abstract

Single crystals of L-argininium dinitrate (LADN), a semiorganic nonlinear optical (NLO) material have been successfully grown by slow solvent evaporation technique. Good optical quality single crystals with dimensions up to $28 \times 8 \times 1\,mm^3$ were obtained. The crystals were characterized by optical absorption spectrum, FTIR and X-ray diffraction studies. The optical absorption spectrum shows that the absorption in LADN is nearly equal to zero in the entire visible region. The thermal stability of the crystal was studied by DTA and TGA.

Keywords: A1. Optical absorption; A1. Slow evaporation; A1. Thermal stability; B1. Analogs of LAP; B2. Nonlinear optical materials

1. Introduction

The invention of L-arginine phosphate monohydrate (LAP) by Xu et al. [1] enhanced the search for new materials in the single crystalline form to fulfill the needs in the field of nonlinear optics. Compared with potassium dihydrogen phosphate (KDP), LAP has larger nonlinearity (>1 pm/V), higher damage threshold ($>15\,J/cm^2$ at 20 ns) and less deliquescence [2–4]. Single crystals formed by amino acids such as L-arginine, L-histidine, etc., are found to be promising nonlinear optical (NLO) materials [5,6]. The widest search for new compounds and crystals of LAP analogs were carried out by reacting arginine with equimolar amounts of various acids. In the case of Arg · HNO_3, it precipitated as fine non-crystalline powder [7]. Petrosyan et al. have reported a new class of arginine compounds with composition Arg · 2Ax (were Ax is an inorganic or organic acid) and the XRD values were determined [8]. Ramasamy et al. have also determined the structure of L-argininium dinitrate (LADN) and reported that the diprotonated argininium molecule is linked by a strong hydrogen bond to the nitrate anion [9]. Recently, the crystallographic studies done by Terzyan et al.

*Corresponding author. Tel.: +91 4422490490; fax: +91 4428175566.
E-mail address: psagayaraj@hotmail.com (P. Sagayaraj).

0022-0248/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jcrysgro.2005.01.045

proved that L-arginine · $2HNO_3$ belongs to monoclinic unit cell with $P2_1$ space group [10]. One such compound, LADN is synthesized and characterization studies are reported.

Our attempt to obtain bulk crystals of Arg · $2HNO_3$ from 1:2 ratio was found to be difficult but we were successful in growing crystals of size $29 \times 8 \times 1\,mm^3$ from 1: 4 ratio. From the structural point of view, L-Arg · $2HNO_3$ crystallizes in the monoclinic system whose lattice parameters are $a = 7.754\,Å$, $b = 7.286\,Å$, $c = 11.673\,Å$, $\alpha = \gamma = 90^\circ$, $\beta = 92.6^\circ$ with space group of $P2_1$. It was found that the second harmonic generation (SHG) signals coming from crystals with $P2_1$ symmetry were much more intense than those from crystals with symmetry $P2_12_12_1$. In addition, the $P2_1$ and P_1 space groups allow non-critical phase matching while in case of $P2_12_12_1$, this is impossible [8].

This paper deals with the growth of L-arginine · $2HNO_3$ crystal and the characterization studies such as single crystal XRD, FTIR, optical absorption, TGA–DTA and morphology. The morphology, thermal analysis and optical transmittance property of the LADN crystals are reported for the first time. The NLO property of the crystals has been confirmed by Kurtz SHG test.

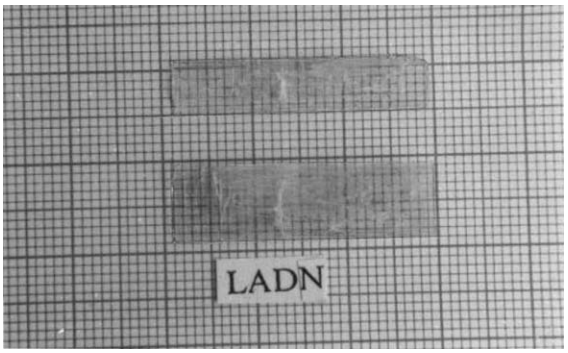

Fig. 1. Photograph of as-grown single crystals of LADN.

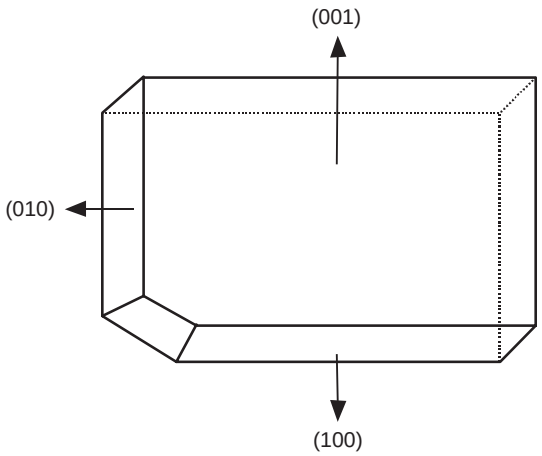

Fig. 2. Typical habit of LADN single crystal.

2. Experimental procedure

Appropriate amount of high-purity L-arginine (Merck 99%) and nitric acid with water were used to prepare the solution of LADN. The following is the reaction:

$$(NH_2)NHCNH(CH_2)_3CH(NH_2)COOH + 4HNO_3 \rightarrow (H_2N)_2^+CNH(CH_2)_3CH(NH_3)^+COOH(NO_3)_2^- + 2HNO_3$$

Seed crystals were formed due to spontaneous nucleation. Transparent good quality seed crystals were used for growth experiments. The growth period of LADN crystals was 30 days. Fig. 1. shows the photograph of as-grown crystals of LADN, grown by the slow evaporation technique at room temperature. The optical absorption spectrum was recorded in the range of 200–800 nm. The X-ray data were collected on an automatic X-ray diffractometer (MESSRS ENRAF NONIUS, The Netherlands). DTA and TGA thermal studies were also carried out for the grown crystal. The FTIR spectrum was recorded in the range of 4000–450 cm^{-1}. The SHG effect was measured using a Nd:YAG-Q switched laser. The morphology of the crystal is depicted in Fig. 2.

3. Characterization

3.1. Single crystal XRD

The X-ray data were collected using an automatic diffractometer. The structure was solved by

the direct method and refined by the full matrix least-squares technique using the SHELXL program. The calculated lattice parameter values are $a = 7.7532\,\text{Å}$, $b = 7.2779\,\text{Å}$ and $c = 11.6754\,\text{Å}$ with $\alpha = \gamma = 90^\circ$ and $\beta = 92.7^\circ$. The cell volume is found to be $658.02\,\text{Å}^3$. The XRD data prove that the LADN crystal is monoclinic in structure with space group of $P2_1$. The XRD data of the sample are in good agreement with the reported values and thus confirm the grown crystal [9,10]. The morphology study indicates that the prominent face of the crystal is (0 0 1).

3.2. Fourier transform infrared (FTIR) spectroscopic analysis

The FTIR spectral analysis of LADN was carried out between 4000 and $450\,\text{cm}^{-1}$. The resulting spectrum is shown in Fig. 3.

In the high-energy region, there is a broad band between 2100 and $3500\,\text{cm}^{-1}$. There are intense sharp peaks in this band at 3457, 3331.6, 3222.8 and $3071.6\,\text{cm}^{-1}$ due to N–H and O–H(–COOH) vibrations. The involvement of NH_3^+ in hydrogen bonding is evident by the fine structure of the band in the lower-energy region. The CH stretching vibration of the methylene group is observed at $2925.2\,\text{cm}^{-1}$. The overtone region 1900–$2100\,\text{cm}^{-1}$ contains a prominent band at $2062.7\,\text{cm}^{-1}$. The C═O stretch of COOH seems to have an intense sharp peak at $1745.2\,\text{cm}^{-1}$.

The peaks at 1685.6, 1656.2 and $1637.7\,\text{cm}^{-1}$ are due to asymmetrical NH_3^+ bending mode. The well-resolved sharp peak at $1536.2\,\text{cm}^{-1}$ is due to symmetrical NH_3^+ bend. The CH_2 bending modes are observed at 1384.6 and $1453.7\,\text{cm}^{-1}$. The NO_3^- vibrations produce characteristic peaks at 1320.3, 1112.1 and $822.3\,\text{cm}^{-1}$. These vibrations clearly demonstrate the existence of L-arginine in its salt form with nitric acid.

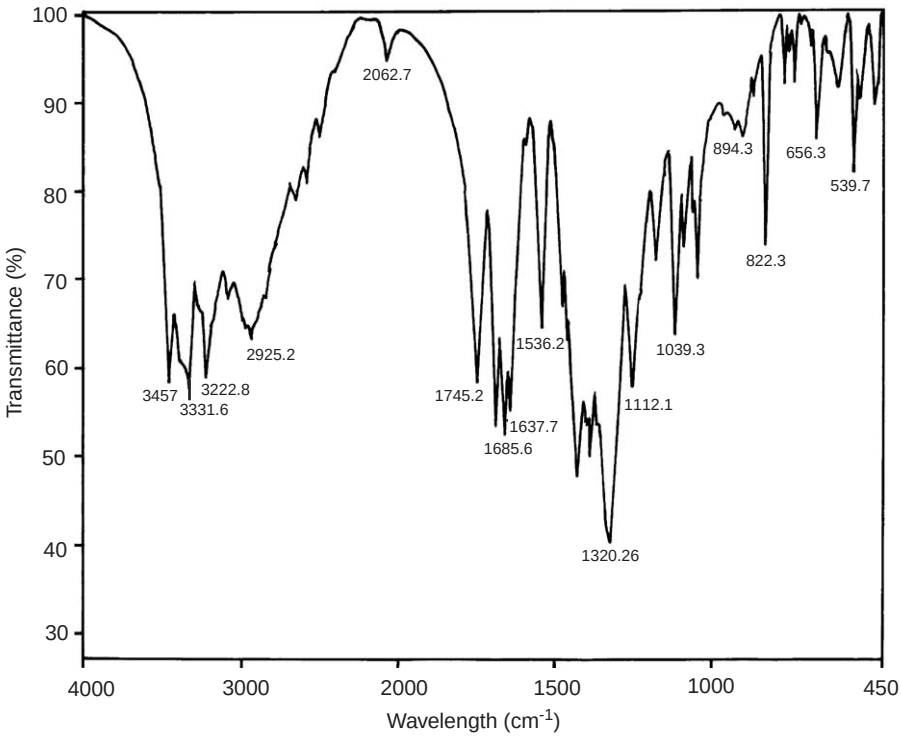

Fig. 3. FTIR spectrum of LADN single crystal.

3.3. Optical absorption spectrum

The optical absorption spectral analysis of LADN was carried out between 200 and 800 nm. As the salt is colourless, its absorption is nearly equal to zero in the entire visible region. This is the most desirable property of the crystals used for NLO applications (Fig. 4).

3.4. NLO studies

Kurtz SHG test performed on LADN crystal confirmed the second harmonic signal generation in the sample by the emission of green radiation.

3.5. Thermogravimetric analysis

The thermogravimetric analysis of LADN was carried out between 28 and 1200 °C at a heating rate of 10 °C/min. The experiment was performed in nitrogen atmosphere. The resulting thermogram is shown in Fig. 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 and 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%.

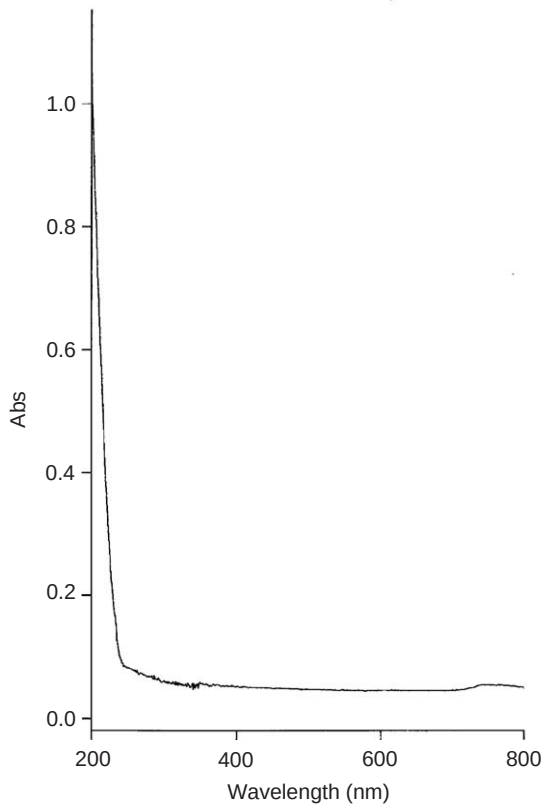

Fig. 4. Optical absorption spectrum of LADN single crystal.

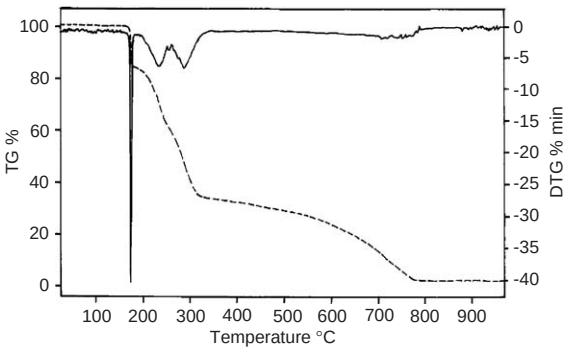

Fig. 5. TGA curve of LADN single crystal.

3.6. Differential thermal analysis

The DTA of LADN was carried out between 28 and 1200 °C in the nitrogen atmosphere at a heating rate of 10 °C/min. The resulting DTA trace is shown in Fig. 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. reported 130 °C as the melting point of LADN but the melting point of the crystal was actually found to be 152 °C in the present study. 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

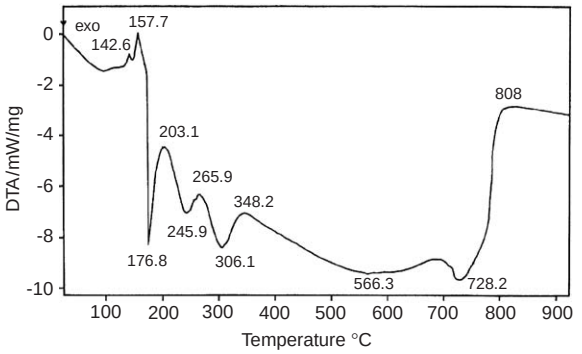

Fig. 6. DTA curve of LADN single crystal.

more endotherms between 200 and 350 °C due to the decomposition of the residue in two stages. Hence, from this study, it can be said that 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.

4. Conclusion

Single crystals of L-argininium dinitrate (LADN) were grown by the slow evaporation technique. The (0 0 1) plane seems to be the dominant face of the grown crystals. The FTIR studies confirm the existence of L-arginine in its salt form with nitric acid. The optical absorption studies confirm the suitability of the crystals for NLO application. From the TGA, it is estimated that the sample is stable up to 130 °C. Further studies are in progress and will be reported soon.

Acknowledgements

The authors are thankful to the Department of Physics, Loyola College for the help offered in conducting experiments. We specially thank Dr. Babu Varghese, SAIF, IIT, Chennai, Dr. M. Palanichamy, Anna University, Chennai and Dr. P. Ramasamy, Crystal Growth Centre for their continuous help and constant encouragement.

References

[1] D. Xu, M. Jiang, X. Tan, Acta Chem. Sinica 41 (1983) 570.
[2] T. Sasaki, A. Yokotani, K. Fujioka, T. Yamanaka, S. Nakai, Technol. Rep. Osaka Univ. 39 (1989) 25.
[3] D. Eimerl, S. Velsko, L. Davis, F. Wang, G. Loiacona, G. Kennedy, IEEE J. Quantum Electron. QE-25 (1989) 179.
[4] A. Yokotani, T. Sasaki, K. Yoshida, S. Nakai, Appl. Phys. Lett. 55 (1989) 2692.
[5] R. Ittyachan, P. Sagayaraj, J. Crystal Growth 249 (2003) 557.
[6] J. Packiam Julius, S.A. Rajasekar, A. Joseph Arul Pragasam, V. Joseph, P. Sagayaraj, Mater. Sci. Eng. B 107 (2004) 259.
[7] S.B. Monaco, L.E. Davis, S.P. Velsko, F.T. Wang, D. Eimerl, A. Zalkin, J. Crystal Growth 35 (1987) 252.
[8] A.M. Petrosyan, R.P. Sukiasyan, H.A. Karapetyan, S.S. Terzyan, R.S. Feigelson, J. Crystal Growth 213 (2000) 103.
[9] S. Ramasamy, B. Sridhar, V. Rama Krishnan, R.K. Rajaram, Acta Crystallogr. E 57 (2001) 0872.
[10] S.S. Terzyan, H.A. Karapetyan, R.B. Sukiasyan, A.M. Petrosyan, J. Mol. Struct. 687 (1–3) (2004) 111.