Indian Journal of Pure & Applied Physics
Vol. 45, June 2007, pp. 524-528

Growth, optical and thermal studies of L-arginine perchlorate—A promising non-linear optical single crystal

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Received 11 July 2006; revised 5 December 2006; accepted 7 February 2007

Optically good quality single crystal of L-arginine perchlorate (abbreviated as LARPCL), a promising analog of LAP was successfully grown by slow solvent evaporation technique at room temperature. The grown crystals were characterized by single crystal XRD, FTIR, FT-Raman, optical absorption and SEM studies. The thermal stability of the crystal was studied by TG, DTA and DSC analysis. The scanning electron microscopy (SEM) provides information about the surface morphology of the sample. The SHG efficiency is estimated using Kurtz powder method.

Keywords: Characterization, Growth from solution, X-ray diffraction, Non-linear optical crystal, Thermal analysis, L-arginine perchlorate

IPC Code: C30B

1 Introduction

Non-linear optical materials will be the key elements for future photonic technologies based on the fact that photons are capable of processing information with the speed of light. Due to this fact, the rapid development of optical communication systems has led to a demand for non-linear optical materials of high structural and optical quality[1,2]. L-arginine phosphate (LAP) is a new material first discovered by Chinese researchers[3] in 1983. The crystal structure of LARPCL was first determined by Srinivasan and Rajaram[4]. Monaco *et al.* [5], Petrosyan *et al.*[6], Ittyachan and Sagayaraj[7] and Pragasam *et al.*[8]. have revealed the suitability of L-arginine family crystals for their non-linear optical properties and applications. Hence, LAP analogs are potential candidates to replace KDP for frequency conversion of infrared lasers. Therefore, crystals of L-arginine perchlorate are an interesting semi-organic non-linear optical material and are selected for the present study.

From the structural point of view, LARPCL crystallizes in orthorhombic system with space group $P2_12_12_1$. The cell parameters[4,5] are a=13.854 Å, b=16.573Å, c=5.083Å and $\alpha = \beta = \gamma = 90^\circ$. The SHG effect of the crystal has been confirmed by Kurtz powder technique[9]. In the present paper, bulk single crystals of LARPCL are grown and characterized by optical, thermal and scanning electron microscopy (SEM) studies. Characterization techniques such as FT-Raman, optical absorption, DSC and SEM have been employed to study such materials.

2 Experimental Details

2.1 Synthesis and crystal growth

LARPCL was synthesized from L-arginine (Merck-99%) and perchloric acid (Merck-70%) taken in equimolar ratio. The calculated amounts of the reactants were thoroughly dissolved in deionized water and stirred well for about 12 h. This was then filtered to remove suspended impurities and allowed to crystallize. Seed crystals were formed due to spontaneous nucleation. Optically transparent good quality seed crystals with perfect shape and free from defects were used for growth experiments. The seeds were suspended in the mother solution with nylon thread and the growth was achieved by slow solvent evaporation technique at a constant temperature of 305 K. In the present study, single crystal of size 20.0 × 6.0 × 4.0mm^3 was grown in a period of 15 days. Fig. 1 shows the photograph of as grown crystals of LARPCL.

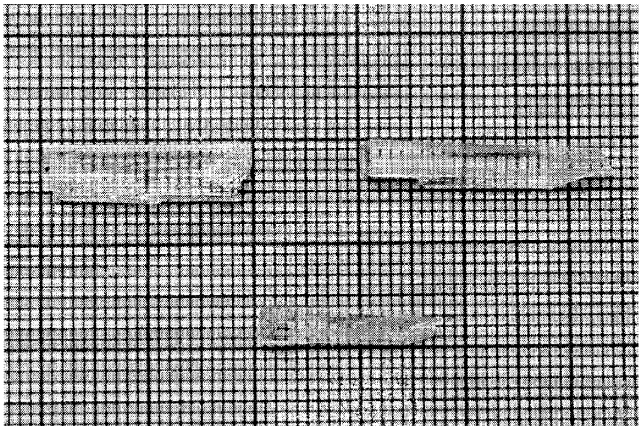

Fig. 1—Photograph of as grown crystal of LARPCL

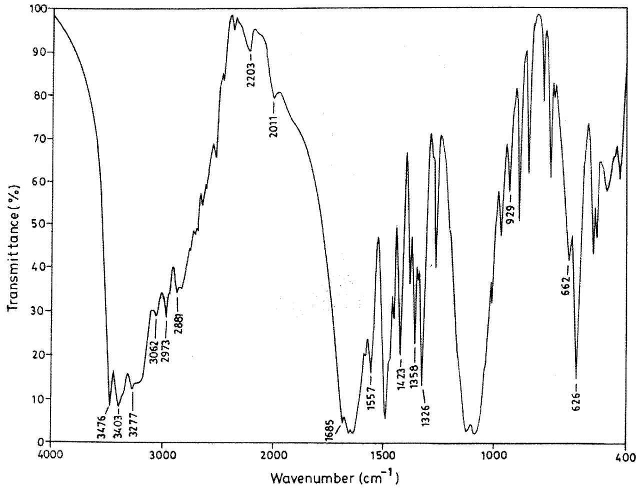

Fig. 2—FTIR spectrum of LARPCL single crystal

Table 1—Crystal data of LARPCL crystal

Empirical formula	$C_6H_{15}N_4O_6Cl$
Formula weight	274.66
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a (Å)	5.0840
b (Å)	13.8296
c (Å)	16.5681
α	90°
β	90°
γ	90°
Volume (Å^3)	1164.88
Z	4

2.2. Characterization

In order to obtain the crystal data of LARPCL crystals, single X-ray diffraction studies were carried out using ENRAF NONIUS CAD4-F single X-ray diffractometer with MoK_α (λ= 0.71073Å) radiation. The various functional groups present in LARPCL crystal were identified and confirmed by the FT-IR study. The spectrum was recorded in the range 4000-400 cm^{-1} using BRUKER IFS-66V spectrometer by KBr pellet technique. FT-Raman spectrum was recorded in the range 50-3500 cm^{-1} using BRUKER FRA 106 FT-Raman spectrometer. The UV-Vis-NIR analysis of LARPCL crystal was carried out between 200 and 2000 nm covering the entire near ultra violet, visible and near infrared regions, using the VARIAN CARY 5E model spectrophotometer. The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of LARPCL crystal was carried out using Perkin-Elmer TGA-7 and Perkin-Elmer DTA-7, respectively in the temperature range 30-600°C. The DSC analysis was done using the instrument NETZSCH STA 409C between 30 and 330°C. The surface morphology of the as grown samples of LARPCL was investigated using a JEOL/EO-JSM-5610 scanning electron microscope .

3 Results and Discussion

3.1 Single crystal XRD

The single crystal XRD data of LARPCL crystal indicates that it crystallizes in orthorhombic system with $P2_12_12_1$ space group. The structure was solved by the direct method and refined by the full matrix least-square technique using the SHELXL program. The calculated lattice parameter values are *a* = 5.0840Å, *b* = 13.8296Å and *c* = 16.5681Å. Volume of the unit cell^3 = 1164.88Å· The crystal data values are listed in Table 1. The single crystal XRD results are in good agreement with the reported values and thus confirm the grown crystal[4,5].

3.2. FT-IR analysis

The middle IR spectrum of LARPCL is shown in Fig. 2. The N-H and O-H vibrations appear as intense broad envelope in the higher energy region with maxima at 3746, 3403 and 3277 cm^{-1}. The former two vibrations are assigned to O-H stretch and the later one to N-H vibration. The C-H vibrations at 2973 cm^{-1} and 2881 cm^{-1}, are clearly seen. In addition, there are clear hyperfine structure bands in the lower energy portion of the envelope, and these are assigned

Table 2—FT-IR spectral assignments of LARPCL single crystals

Wavenumber (cm^{-1})	Band assignments
3476, 3403	O-H stretching vibration
3277, 3062	N-H stretching vibration
2973, 2946, 2881	C-H stretching vibration
2011	Combination of NH_3^+ torsional oscillation and its symmetrical bending
1685,1655	C=O stretch of $–COO^-$
1636	NH_3^+ asymmetrical bending
1581	N-H bending (scissoring)
1490	NH_3^+ symmetrical bending
1452	CH_2 in-plane bending or scissoring
1381,1358	CH_2 bending
1326	CH_2 wagging
1264	$-COO^-$ stretching
1009,929	$-ClO_4^-$ vibration
777	scissoring mode of COO^-
626	O-H out-of-plane deformation, $-ClO_4^-$ vibration
550,533	Torsional oscillation of NH_3^+
430	$-ClO_4^-$ vibration

Table 3—FT-Raman spectral assignments of LARPCL single crystal

Wavenumber (cm^{-1})	Band assignments
3385,3268,3168	N-H stretching vibration
2938	C-H stretching
1564	NH_3^+ bending
1329	CH_2 wagging
940	$-ClO_4^-$ vibration
849	C-C stretching
751	NH_2 out-of-plane bending
634	$-ClO_4^-$ bending vibration

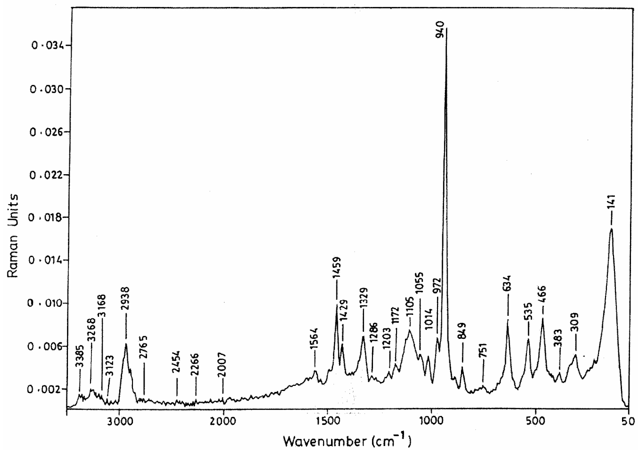

Fig. 3—Raman spectrum of LARPCL single crystal

to hydrogen bonding of N-H and O-H grouping. Generally, hydrogen bonding of any group can broaden the peak due to its group vibration. In addition, there will be fine structure (partly resolved peaks) in the lower energy region of the broadened peak. Actually hydrogen bonding decreases the energy of the group vibration. The intense band comprising of peaks due to asymmetric –COOH and $–NH_3^+$ vibrations produces a maximum at about 1650 cm^{-1}. The symmetric vibrations of $–NH_3^+$ and –COOH groups are positioned at 1490 and 1423cm^{-1}.

The CH_2 bending vibrational peaks[8] are seen at 1452, 1381, 1358 and 1326cm^{-1}. The presence of $-ClO_4^-$ is clearly evident by its characteristic peaks at about 1100 cm^{-1} (ν_3) (F_2), 929 cm^{-1} (ν_1) (A_1), 626 cm^{-1} (ν_4) (F_2) and finally 430 cm^{-1} (ν_2) (E). The existence of arginine perchlorate ($C_6H_{15}N_4O_2.ClO_4^-$) is clearly evident from its characteristic -O-H vibrations (3473 cm^{-1} and 3403 cm^{-1}) and ClO_4^- vibrations at 1100 cm^{-1} (very intense), 929 cm^{-1}, 626 cm^{-1} (very sharp) and 430 cm^{-1}. The FT-IR spectral assignments of LARPCL single crystal is shown in Table 2.

3.3 FT-Raman studies

The FT-Raman spectrum of LARPCL single crystal covering the region 50-3500 cm^{-1} is shown in Fig. 3. The N-H vibrations appear very weak in the higher energy region. The C-H vibrations occur at 2938 cm^{-1}. The vibrations of $–NH_3^+$ are seen at 1459 cm^{-1} and 1429 cm^{-1}. The peak at 1329 cm^{-1} is due to $–CH_2$ bending. The COO^- vibrations give a cluster of peaks between 1000 cm^{-1} and 1225 cm^{-1}. The ClO_4^- vibration appears as intense sharp peak[9] at 940 cm^{-1}. The torsional oscillation of NH_3^+ is assigned to the peak at 535 cm^{-1}. The peak at 634 cm^{-1} is assigned to ClO_4^- bend. The FT-Raman spectral assignments of LARPCL single crystal is shown in Table 3.

3.4. Optical absorption studies

The optical absorption spectrum of the compound LARPCL was recorded in the range 200-2000 nm and is shown in Fig. 4. The absorbance is almost zero in the UV and the entire visible region, which is an interesting observation in this material. The very low value of absorbance below 900 nm is an advantage and is a desirous property of the materials for NLO applications.

3.5. NLO studies

In order to confirm the NLO property, the grown specimen was subjected to NLO test using high intensity Nd:YAG laser. The input laser beam was directed on the LARPCL powder to get maximum second harmonic generation efficiency. The emitted light passed through an IR filter was measured by means of a detector and oscilloscope assembly. The output could be seen as a bright green light emission from the sample. The second harmonic generation efficiency was found to be 0.2 with respect to urea. This value is slightly higher than that reported by Mallik and Kar[12], which was found to be 0.13 with respect to urea. The enhanced value of efficiency in the present work may be attributed to the relatively large size and good optical grade crystals grown under optimized growth conditions.

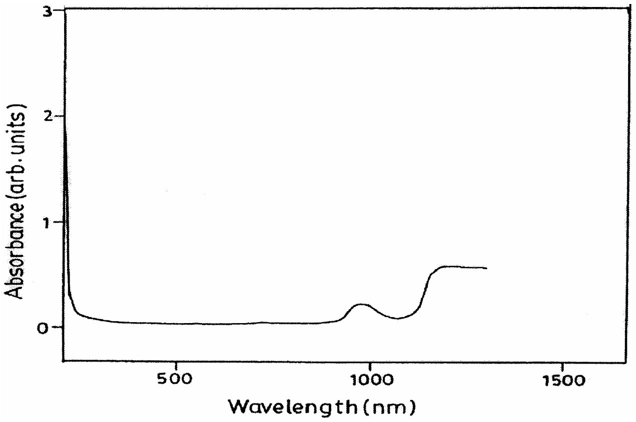

Fig. 4—UV-Vis-NIR spectrum of LARPCL single crystal

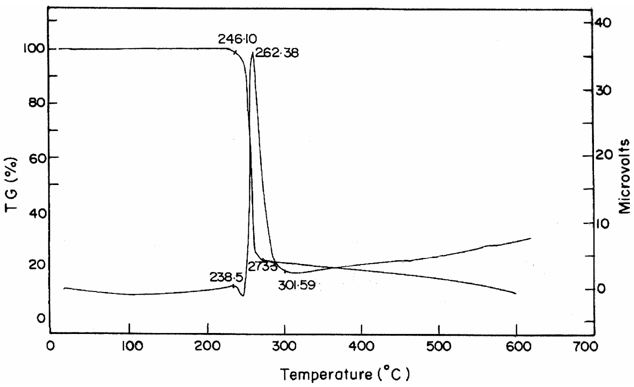

Fig. 5—TG-DTA curves of LARPCL single crystal

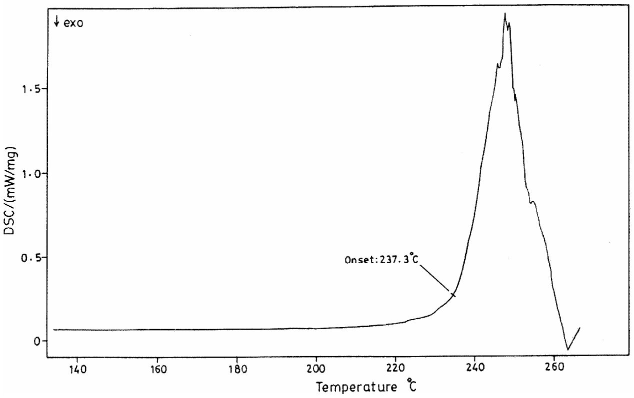

Fig. 6—DSC curve of LARPCL single crystal

3.6. Thermal analysis

The TGA and DTA of LARPCL crystal were carried out between 303 K and 873 K in nitrogen atmosphere. The heating rate was maintained at 20 K/min. The TGA and DTA traces are shown in Fig. 5. The TGA curve indicates that there is a major weight loss starting at about 519.1 K and ending at 546.3 K due to elimination of volatile substances in the compound, probably carbon dioxide, ammonia and oxides of chlorine. Since this temperature is beyond 373 K, there is no evidence for any entrapped water in the crystal lattice or any physically adsorbed water on the surface of the crystal.

The DTA trace shows an endothermic peak at about 511.5 K which corresponds to the melting point of the compound. The melting point of LARPCL crystal was separately verified by melting point apparatus. This is immediately followed by a sharp endotherm at 535.38 K, coinciding with the major weight loss observed due to decomposition as shown in TGA trace.

The DSC analysis of LARPCL was carried out between 313 and 633 K at a heating rate of 5 K/min in nitrogen atmosphere and is shown in Fig. 6. The DSC trace indicates a sharp endotherm starting at 510.3 K which coincides very well with the melting point of the sample. Also, it is found that there is no endo or exotherm up to 493 K, proving the absence of water of crystallization in LARPCL crystals. This observation is similar to that found in TGA trace. The results indicate the thermal stability of LARPCL up to 493 K and establish its suitability to withstand high temperatures in laser experiments.

3.7 SEM studies

Fig. 7 (a and b) shows the SEM micrographs of LARPCL corresponding to different magnification and the surface morphology of the epilayers which were found to have twins or clusters in the single crystal. In Fig. 7 (b) the surface appears to be smooth and a number of micro crystallites were present on the surface.

4 Conclusion

Good optical quality LARPCL single crystals were grown by slow solvent evaporation technique. The

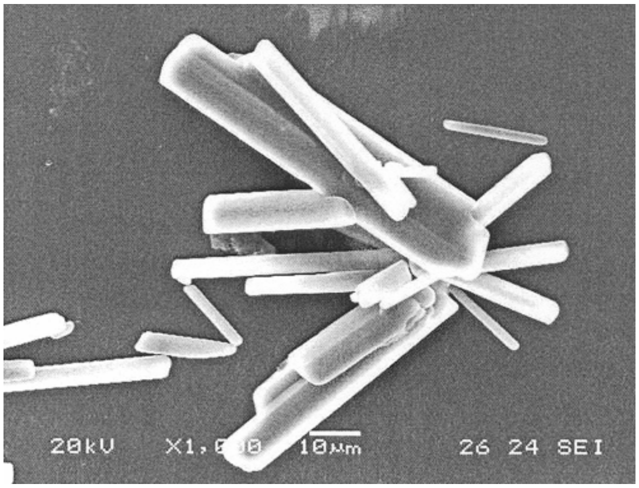

Fig. 7(a)—SEM micrograph of LARPCL single crystal showing clusters

Fig. 7(b)—SEM micrograph of LARPCL single crystal showing microcrystallites

lattice parameters were found by single crystal XRD. Optical studies like FT-IR, FT-Raman and optical absorption analyses suggest that this material is desirable for applications in the field of photonics. TGA and DSC analyses confirmed that there is no water of crystallization present in LARPCL and it is stable up to 493 K. Second harmonic efficiency is found to be 0.2 times that of urea.

Acknowledgement

The authors acknowledge Dr M Palanichamy (Department of Chemistry, Anna University, Chennai 600 025) for useful discussions and constant encouragement. The authors also thank Dr V Damodara Das (Department of Physics, Indian Institute of Technology, Chennai), Dr Babu Varghese (SAIF, Indian Institute of Technology, Chennai), for their valuable help. One of the authors (S Aruna) thanks University Grants Commission, New Delhi, for granting UGC tenth plan FIP teacher fellowship.

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