ISSN 1996-3343

# Asian Journal of Applied Sciences

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Asian Journal of Applied Sciences 9 (1): 23-29, 2016
ISSN 1996-3343 / DOI: 10.3923/ajaps.2016.23.29


# Optical Characterizations of L-Alaninium Maleate Single Crystals

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## ABSTRACT

The innovation, with an eye for application, has been the key to successful crystal harvesting. It is realized that crystalline material is intrinsically applied and basic research in this area needs to be directed and motivated by specific applications in technology. Combination of aminoacids with organic materials gets increased efficiency made this study of optical characterization of l-alaninium maleate-a novel organic NLO crystal. The single crystals are grown by slow evaporation technique by mixing L-Alanine with maleic acid in the ratio 1:0.25, 1:0.5, 1:0.75, 1:1. Single crystal X-ray diffraction study is compared with powder X-ray diffraction study. The FTIR spectrum is drawn for the crystals and their functional groups were determined. The UV-Vis-NIR spectrum shows less optical absorption in the entire visible region. The band gap energy of the crystals were calculated. Non-Linear optical efficiency was evaluated by Kurtz and Perry powder technique using Q-switched Nd-YAG laser.

**Key words:** Characterization, X-ray diffraction, NLO materials, optical absorption

## INTRODUCTION

In recent years, many significant achievements have been occurred in the field of nonlinear optics because of the development of new nonlinear optical (NLO) crystals of both organic and inorganic type (Prasad and Williams, 1991; Nalwa and Miyata, 1991). The main advantage of the organic materials is the tailor made flexibility (molecular engineering) in comparison with the inorganic counterparts. The amino acid complexes have received much attention because they proved to be useful in nonlinear optical application.

Considerable efforts have been made to combine the amino acids with effective organic and inorganic materials in order to produce the novel materials to challenge the existed NLO materials like potassium dihydrogen phosphate (KDP), lithium niobate, potassium niobate and potassium borates, etc. The crystals like LTA (Kumar *et al*., 2005). LAHCL (Meera *et al*., 2004) and LHFB (Aggarwal *et al*., 1999) etc. are good examples of the amino acid related semi organic materials. Most materials with high Second Harmonic Generation (SHG) efficiency show significant absorption in the blue or violet region. Researchers have recently demonstrated efficient blue-light generation below 400 nm using highly efficient organic single crystals (Hornak *et al*., 1992). Such organic materials may be used in terabit optical data storage applications. Efficient nonlinear signal processing in the optical frequency domain requires the development of new families of materials. The search for more efficient NLO materials has evinced great interest in organic materials with nonlinearities, in some cases, one order of magnitude above those of inorganic

compounds. Other advantages of these materials are their high flexibility in terms of molecular structure, their comparatively high optical damage threshold, low cost and their short response time to optical excitation (Boomadevi *et al*., 2004). The salts of weak carboxylic acid (maleic acid) with amino acids, viz., L-alaninium maleate (Natarajan *et al*., 2006) and L-arginine maleate were synthesized and reported recently as good NLO materials. Thus, the L-Alaninium maleate LAMA an aromatic organic compound is another such example to create interest in the study to evolve its optical characterization.

## MATERIALS AND METHODS

In the present study, L-alanine (AR) is doped with maleic acid (AR) in different concentration and synthesized by Slow Evaporation method (Kumar *et al*., 2008; Chitra and Palaniswamy, 2010; Bright and Freeda, 2010; Lucia Rose *et al*., 2010). The grown crystals were subjected to Optical characterization studies such as single crystal XRD (Dhanuskodi and Vasantha, 2004) FTIR, optical absorbance were done (Prabha and Palaniswamy, 2010). Kurtz and Perry SHG test confirms the NLO property of the grown crystals (Franken *et al*., 1961; Bloembergen, 1965).

Pure L-alanine lattice parameter values and its pattern were compared with JCPDS (Joint Committee on Powder Diffraction Standards) file no. 28-1508. Pcpdfwin and National Bureau of Standards there by studied its dopant intrusion in the grown crystals.

**Synthesis:** L-alaninium maleate (LAMA) was synthesized from L-alanine ($CH_3CHNH_2COOH$) and maleic acid ($C_4H_4O_4$), both were mixed in different molar ratio, 1:0.25, 1:0.50, 1:0.75 and 1:1 (LAMA).

**Instrumentation:** The single crystal X-ray data were collected using an automatic X-ray diffractometer (MESSRS ENRAF NONIUS, The Netherlands) with $MoK_\alpha$ ($\lambda$ = 0.717 Å) radiation. The freshly ground powder samples of LAMA crystals were subjected to Powder X-Ray Diffraction (PXRD) analysis, using an X-ray powder diffractometer, PANalytical with scintillation counter and monochromated Cu $K_\alpha$ ($\lambda$ = 1.54056 Å) radiation. The FT-IR spectrum was recorded in the range of 4000-450 $cm^{-1}$ using BRUKER IFS 66V FT-IR SPECTROMETER. The optical absorption spectrum was recorded in the range of 190-800 nm using VARIAN CARY 5E UV-Vis-NIR SPECTROPHOTOMETER. The NLO efficiency of LAMA crystal were evaluated by Kurtz and Perry powder technique using Q-switched Nd:YAG laser.

## RESULTS AND DISCUSSIONS

**Single crystal XRD analysis:** The single crystal XRD data of the LAMA crystals with different concentration of maleic acid are presented in Table 1. It is observed that the different concentration of maleic acid mixed in LAMA crystals have orthorhombic structure with a space group of $P2_12_12_1$, which is recognized as non-centrosymmetric, thus satisfying one the basic and essential material requirements for the SHG activity of the crystal (Zyss *et al*., 1984). The lattice parameters (a, b and c) and unit cell volume of the LAMA crystals increases with the increase of concentration of maleic acid in LAMA crystal (Raj and Madhavan, 2011).

**Powder X-ray diffraction analysis:** The XRD powder pattern has been indexed and the lattice parameters are evaluated. The Bragg's diffraction peaks were indexed for the orthorhombic system

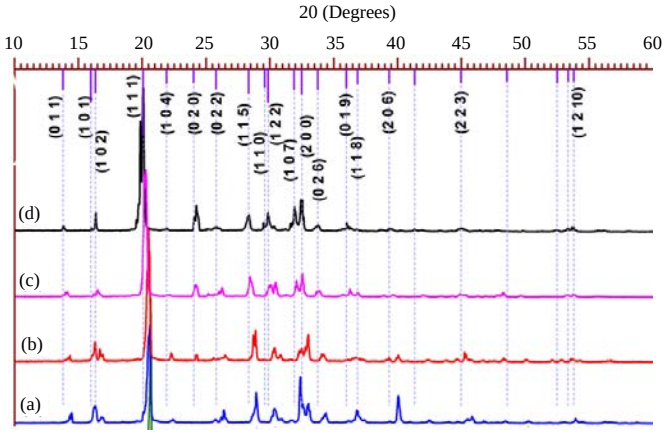


Fig. 1: Powder XRD pattern

Table 1: Lattice parameters from single crystal XRD

| Data | LA $(MA)_{0.25}$ | LA $(MA)_{0.50}$ | LA $(MA)_{0.75}$ | LAMA |
|---|---|---|---|---|
| a (Å) | 5.9833 | 5.6547 | 5.6214 | 5.5953 |
| b (Å) | 12.1641 | 7.4786 | 7.5317 | 7.3682 |
| c (Å) | 6.2547 | 22.8352 | 22.9621 | 23.7216 |
| V (Å$^3$) | 455.226 | 965.683 | 972.185 | 977.977 |
| α$^o$ | 90 | 90 | 90 | 90 |
| β$^o$ | 90 | 90 | 90 | 90 |
| γ$^o$ | 90 | 90 | 90 | 90 |
| Crystal system | Orthorhombic | Orthorhombic | Orthorhombic | Orthorhombic |
| Space group | $P2_12_12_1$ | $P2_12_12_1$ | $P2_12_12_1$ | $P2_12_12_1$ |

Table 2: Lattice parameters from powder XRD

| | | Calculated lattice parameters | | | |
|---|---|---|---|---|---|
| Concentration of maleic acid in LAMA (mole) | Sample name | a (Å) | b (Å) | c (Å) | Volume (Å$^3$) |
| 0.25 | $LA(MA)_{0.25}$ | 6.0139 | 12.01260 | 6.3459 | 458.441 |
| 0.50 | $LA(MA)_{0.50}$ | 5.7953 | 7.95220 | 20.9764 | 966.705 |
| 0.75 | $LA(MA)_{0.75}$ | 5.7661 | 7.62470 | 21.1457 | 973.631 |
| 1 | LAMA | 5.6087 | 7.35790 | 23.7341 | 979.464 |
| | | 5.5873$^{\#}$ | 7.3864$^{\#}$ | 23.6879$^{\#}$ | 977.601$^{\#}$ |

#: Indicates lattice parameter values of LAMA crystal from literature (Balasubramanian *et al*., 2009)

with the space group $P2_12_12_1$. The continuous peak shifting rule out the phase separation or separate nucleation of L-Alanine and maleic acid crystals (Fig. 1) with increasing dopant from a to d.

The uniform unit cell volume expansion reveals that concentration of maleic acid play a role in lattice expansion but do not modify the lattice structure of LAMA Table 2.

**FTIR analysis:** The FTIR absorption spectrum of LAMA crystals in the region 4000-450 cm$^{-1}$ is shown Fig. 2 (with increase in dopant from a to d). The NH stretching bond of aromatic compounds is generally observed in a range between 3200 and 3300 cm$^{-1}$. In the present study, it is observed at 3240 cm$^{-1}$. The vibration observed at 1361 cm$^{-1}$ was attributed to C-C stretching vibration. This analysis also indicates that the protonation of carboxyl group in Alanine takes place by maleic acid. The absorptions of LAMA have been compared with those of the L-alanine (Nakamoto, 1985). The

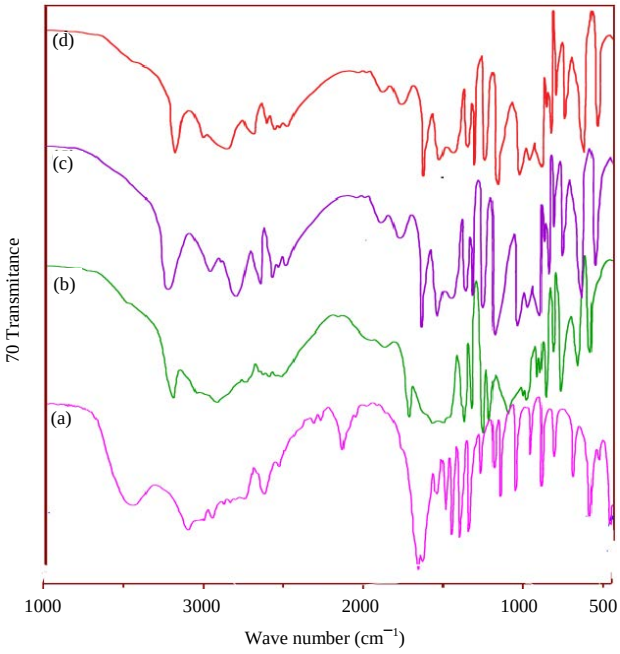


Fig. 2: FTIR Spectrum

Table 3: FTIR band Assignments of LAMA crystals

| | Wave number | | | |
|---|---|---|---|---|
| Assignments | LAMA | LA $(MA)_{0.75}$ | LA $(MA)_{0.5}$ | LA $(MA)_{0.25}$ |
| $NH^{3+}$ symmetric stretching | 3094 | 3092 | 3090 | 3085 |
| N-H symmetric Stretching | 3056 | 3045 | 3015 | 3006 |
| Aliphatic (C-H) stretch (super imposed on N-H stretch) | 2994 | 2994 | 2994 | |
| Aliphatic (C-H ) stretch | 2825 | 2819 | 2815 | 2812 |
| C-H symmetric stretching | 2610 | 2608 | 2602 | 2600 |
| Over tone region with a combination of symmetric $NH^{3+}$ bending and torsional vibrations. | - | - | 2113 | 2113 |
| Asymmetrical $NH^{3+}$ bending | 1629 | 1627 | 1621 | 1621 |
| (C = O ) stretching | 1598 | 1596 | 1590 | 1590 |
| $NH^{3+}$ asymmetric bending | 1525 | 1526 | 1520 | 1518 |
| COO-symmetric stretching | 1462 | 1461 | - | 1455 |
| (C-H) Bending in plane | 1312 | 1309 | 1306 | 1306 |
| C-O-C stretching | 1158 | 1156 | 1153 | 1151 |
| Symmetrical C-O-C stretching | 1114 | 1113 | 1113 | 1113 |
| C-CHO stretching | - | - | 1016 | 1015 |
| O-C-O bending | 779 | 774 | 773 | 773 |
| (C-H) bending | 659 | 655 | 653 | 649 |

observed lower wave number and hence, the lower energy indicate the large hydrogen bonded association of LAMA in the crystal lattice. Table 3 shows the band assignments of LAMA crystals for various concentrations. The shifts in the positions of the characteristic peaks confirm the formation of the compound.

**Optical absorption spectrum analysis:** The optical absorption spectrum of LAMA (with different concentration) is shown in Fig. 3, in the wavelength range 190-800 nm. No absorption is observed in the visible region of the UV-V is spectra which is due to electronic transitions between

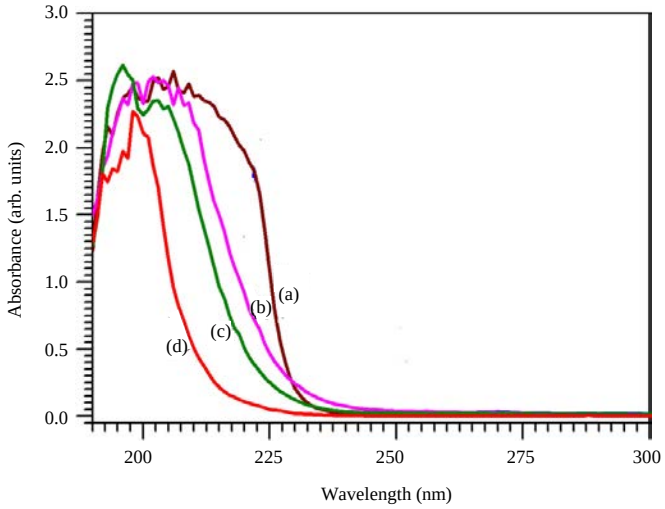


Fig. 3: UV-Vis absorption spectrum

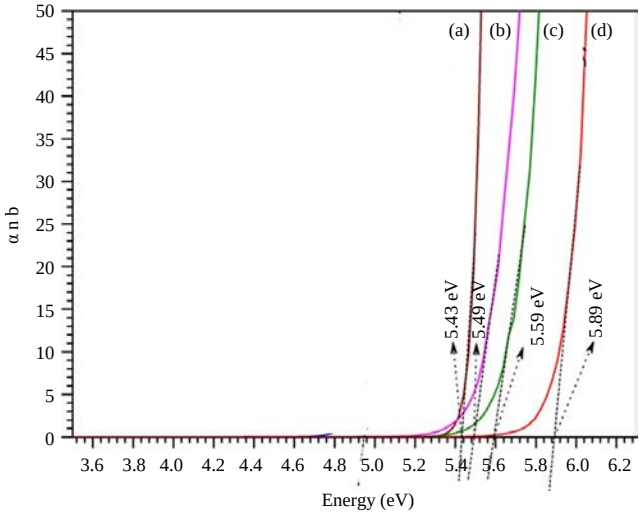


Fig. 4: Plot for Optical band gap

the carboxylate anion ($-COO^-$) and the nitryl cation ($NH_3^+$) (Shakir *et al*., 2009; Misoguti *et al*., 1996). A UV cut-off below 300 nm is sufficiently low for SHG laser radiation at 1064 nm or other applications in the blue region. Optical band gap has been calculated from the UV-V is absorbance data Table 4.

The absence of absorption bands in the visible region and the wide band gap of the grown crystal (Fig. 4) attest to the suitability of the grown crystal for photonic and optical applications (Rao and Smakula, 1965).

**NLO studies:** A high intensity Nd:YAG laser (λ = 1064 nm) with a pulse duration of 8 nsec was passed through the powdered sample. The SHG behavior was confirmed from the output of the laser beam having the green emission (λ = 532 nm). For a laser input pulse of 6.5 mJ, the second

Table 4: Optical bandgap energy and cutoff wavelength of pure LA and LAMA crystal

| Sample name | Optical bandgap energy (eV) | Cutoff wavelength (nm) |
|---|---|---|
| LA $(MA)_{0.25}$ | 5.43 | 228 |
| LA $(MA)_{0.50}$ | 5.49 | 226 |
| LA $(MA)_{0.75}$ | 5.59 | 222 |
| LAMA | 5.89 | 211 |

Table 5: SHG efficiency values of LAMA crystals

| Sample name | Input power (mJ) | Output power (mV) | SHG efficiency (compared with KDP) (times) |
|---|---|---|---|
| LA $(MA)_{0.25}$ | 6.5 | 122.5 | 2.31 |
| LA $(MA)_{0.50}$ | 6.5 | 146.7 | 2.77 |
| LA $(MA)_{0.75}$ | 6.5 | 169.6 | 3.38 |
| LAMA | 6.5 | 218.9 | 4.13 |

harmonic signal (532 nm) of 122.5 and 53 mV were obtained through LAMA and KDP samples, respectively (Table 5). The good second harmonic generation efficiency indicates that the LAMA crystals can be used for applications in nonlinear optical devices.

## CONCLUSION

L-alaninium maleate (LAMA) single crystals were grown by mixing pure L-alanine with maleic acid in the molar concentration 1:0.25, 1:0.50, 1:0.75 and 1:1 and the crystals were grown using slow solvent evaporation technique. These crystals were characterized with single X-ray diffraction analysis and found to be orthorhombic crystal structure with the space group $P2_12_12_1$. The lattice parameters calculated for all the grown crystals were compared with the values with powder X-ray diffraction analysis and finds a perfect matching. The growth rate along the c-axis is large compared to other two crystallographic axes. It is found, among the well developed faces the (111) face is larger in area. It is verified that the increases in volume of the unit cell with the addition of maleic acid identifies its presence in the lattice construction. FTIR transmission spectrum is recorded in the range 4000-450 $cm^{-1}$. The observed lower wave number and lower energy indicates the large hydrogen bonded association of LAMA in the crystal lattice. The vibration observed at1361 $cm^{-1}$ was attributed to C-C stretching vibration. Optical absorption spectrum shows some significant blue shift in the shape and position of the absorption peaks but not affected the optical absorbance in the visible range and a small variation observed in a UV range is due to crystalline perfection of the grown crystals. The optical band gap energy is found to increase with increase of its molar concentration and UV cut off wavelength of these crystal decreases with increasing concentration revealing that the cut off wavelength can be tuned revealing as a potential material for frequency conversion. The nonlinear optical property was confirmed by Kurtz and Perry powder technique. The emission of green radiation confirms the existence of SHG.

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