Appendix
University Grants Commission sponsored Minor Research Project

(MRP(S)-1344/11-12/KLCA003/UGC-SWRO)

Final Report on

SYNTHESIS,GROWTH AND CHARACTERIZATION OF NONLINEAR OPTICAL L-ARGININE DIMALEATE SINGLE CRYSTAL

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October 2012–October 2014

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Introduction

Nonlinear optical (NLO) materials have attracted much attention because of their wide applications in high-speed information processing, laser frequency conversion, optical data storage, signal communications and optical modulating . Organic materials are expected to have relatively strong nonlinear optical properties due to the presence of delocalized p-electrons conjugate system, connecting donor and acceptor group, responsible for enhancing their asymmetric polarizability . This expectation explains extensive search for better NLO materials because of high flexibility in terms of molecular structure, high optical damage threshold, low cost and short response time to optical excitations among organic crystals .L-Arginine is one of the essential amino acids widely distributed in biological substances. It forms a number of salts with organic and inorganic acids showing nonlinear optical properties. L-Arginine maleate dihydrate is one of those L-arginine salts, which is a complex of strong basic amino acid. It is also a nonlinear optical material with second harmonic generation efficiency 1.4 times that of KDP . LAMD crystals are grown from solution by solvent evaporation. The crystal belongs to the triclinic system with space group P1. The growth of high-quality single crystals remains a challenging task for crystal growers. Growth of defect free transparent bulk single crystals along a particular axis is very important for the preparation of functional crystals. For example the conversion efficiency of SHG is always high along the phase matching direction for nonlinear optical crystals. From this point of view, the Sankaranarayanan–Ramasamy (SR) method is a capable method to grow bulk single crystal along a specific orientation . The unidirectional crystal growth method is most suitable for the crystal growth along particular direction. In addition, the unidirectional solution crystallization usually occurs at around room temperature; much lower thermal stress is expected in these crystals over those grown at high temperature . In the present investigation, bulk single crystals of LAMD were grown by the SR method.

Objectives

1. To grow crystals from aminoacids (speciallyL-arginine) which have nonlinear optical property.
2. To grow defect free single crystals along a particular axis this is very important for the prepration of functional crystals. For this Sankaranarayanan-Ramasamy (S-R) method is used.
3. Characterization studies:
    a) XRD- to know the all parameters and structure
    b) FTIR analysis for knowing the functional groups.

c) Uv-vis NIR analysis
d) Microhardness studies.
e) Dielectric measurement
f) Piezoelectric measurement
g) SHG conversion efficiency

Experimental Procedures

1. Material synthesis and purification

Equimolar amount of strongly basic amino acid, L-arginine(Merck, 99%) and weak organic acid, maleic acid (Loba Chemie, 99.5%) were dissolved in double distilled water to synthesize LAMD as per the following reaction.

During this crystallization, L-arginine maleate transformed to its hydrated form with the addition of two molecules of water of crystallization to its crystal lattice. The synthesized material was then purified by repeated recrystallization process and melting point measured was carried out to monitor the purity of the material.

2. Synthesis and crystal growth

LAMD was synthesized by dissolving the equimolar quantities of L-arginine and maleic acid in Millipore water at room temperature. The synthesized LAMD was purified by repeated crystallization process several times before growth. The recrystallization was carried out to minimize the impurities of the raw materials, which in turn enhances the optical quality of the grown crystals. The saturated solution was prepared in accordance with the solubility data . LAMD crystals were grown by slow evaporation solution technique. Cut and polished portion of the LAMD crystal along (0 0 1) face was fixed at the bottom of the ampoule. Slightly under saturated LAMD solution was prepared and slowly poured into the ampoule. The top portion of the ampoule was covered by a plastic sheet with a hole at the center to limit the evaporation. Then, the whole ampoule was kept in the double container using water medium to prevent the fluctuations in temperature.Once the system attains equilibrium, the growth was initiated with a suitable temperature provided by the ring heater at the top of the solution. Top of the growth ampoule was maintained at 38º C for solvent evaporation. The temperature around the growth region is maintained at 34º C for the growing crystals. The experimental conditions were closely monitored and found that the LAMD seed crystal started to grow after 10 days. In a time span of 40 days, a good quality single crystal of LAMD was harvested from the ampoule.

Results and discussion

1. Single crystal X-ray diffraction

From the single crystal XRD measurement, it is found that the grown single crystal belongs to the triclinic system and has a noncentrosymmetric nature with the space group P1. The determined lattice parameters are a=5.259 (3) A˚ , b=8.041 (2) A˚ , c=9.791 (3) ˚A and =106.27 (3)1, =97.24 (3)1, =101.69 (3)1 and volume=381.8 (3) ˚A. The observed values are consistent with the reported literature value.

2. FTIR transmission studies

Fourier transform infrared (FTIR) spectroscopy was used to identify the functional groups present in synthesized material. The characteristic deformation bands of the NH3+ group present in all amino acids appeared at 1520cm−1. Two bands at 566cm−1 and 1186cm−1 corresponding to the torsion and rocking respectively, of the NH3+ group were observed. The combination band in the region 2020–2100cm−1 is due to the combination of NH3+ deformation and NH3+ torsion and is a very good indicator for the identification of the charged NH3+ group. The peaks at 1103cm−1 , 1384cm−1.

Table 1
Calculated and reported lattice parameter values of LAMD.

Lattice parameters	Calculated values	Reported values [11]
a	5.248Å	5.264Å
b	8.054Å	8.039Å
c	9.763Å	9.784Å
	106.45◦	106.19◦
	97.15◦	97.24◦
	101.80◦	101.66◦

Table 2
Assignment of IR band frequencies (cm−1)

Wave number (cm−1)	Assignments
566	Wagging COO−
661	CH2 rocking
690	CN symmetric stretch
866	NH2 rocking
1103	NH3+ rocking, C–N stretching
1186	NH3+ rocking

1384	COO− symmetric stretching
1583	COO− asymmetric stretching
1640	COO− asymmetric stretching
2020–2100	NH3+ deformation combination bandof NH3+ degenerate deformation andNH3+ torsion
3320	H2O symmetric stretching, NH2asymmetric stretch
3480	H2O asymmetric stretching

and 1583cm−1 are assigned respectively to C–N stretching, COO−symmetric stretching and COO− asymmetric stretching bands. The bands at 3398cm−1 are assigned to the presence of water molecule. The peaks between 918cm−1 and 1106cm−1 were assigned to asymmetrical coupled vibrations of maleic acid and l-arginine. Thus by the use of available data on the vibrational frequencies of several amino acids ,the characteristic IR bands for different molecular groups present in the LAMD have been identified and their assignments are given in (Table 2).

3. UV–vis NIR transmittance spectral analysis

The UV–vis NIR spectrum gives limited information about the structure of the molecule because the absorption of UV and visible light involves promotion of the electron in _ and _ orbitals from the ground state to higher energy states .Transmittance spectra are very important for any NLO material because a nonlinear optical material can be of practical use only if it has wide transparency window. To find the transmittance range of LAMD, the optical transmittance spectrum for the wavelengths between 190nm and 1100nm was recorded. A crystal of thickness 2mm was used for this analysis. A graph of transmission versus wavelength is shown in Fig. 3. From the graph, it is evident that LAMD crystal has a UV cutoff around 300nm which is sufficiently lowfor SHG laser radiation at 1064nm or other application in the blue region. It is optically transparent in the UV–vis NIR region with 45% transmission level. There is no considerable absorption of light to any appreciable extent in the visible range of electromagnetic spectrum, which is the intrinsic property of all amino acids .

Piezoelectric measurement

A piezoelectric substance is one that produces an electric charge when a mechanical stress is applied. The piezoelectric property is related to the polarity of the material. The obtained piezoelectric coefficient measurement was carried out for the grown crystals without polishing the crystal. From oscilloscope the output was

obtained directly. The piezoelectric coefficient (d_{33}) was measured in units of pCN^{-1}. The obtained d_{33} value increased from 0.64 pCN^{-1} for SEST-grown LAMD crystal. Higher crystalline perfection may be the reason for the higher piezoelectric values for the SR method grown LAMD crystals.

Dielectric studies

Dielectric properties are related with the electric field distribution within solid materials. Study of dielectric properties provides the quality information of materials. The cut and polished single crystal of LAMD was used for dielectric studies. The sample was electrode on either side with graphite coating to make it behave like a parallel plate capacitor. The capacitance and dielectric loss ($\tan\delta$) of the sample prepared from these crystals were measured as a function of temperature at the frequency of 1 kHz. Fig. shows the variation in dielectric constant with the temperature at 1 kHz. As shown in the figure, the dielectric constants are slightly increased by the temperature variation without distinct anomaly or dispersion. The SR-grown LAMD crystal has a dielectric constant value higher than the dielectric constant of SEST-grown crystal. The dielectric constant of materials is due to the contribution of electronic,ionic,dipolar and space charge polarizations,which depend on the frequencies, all these polarizations are active . From the plot, this is attributed due to the presence of the space charge polarization near the gain boundary interfaces, which depends on the purity and perfection. The space charge polarization is generally active at low frequencies and at high temperature.

Microhardness study

The microhardness testing is the simplest characterization technique that can be best employed to study the mechanical properties of material, such as fracture behavior, yield strength, brittleness index and temperature of cracking . For each load several trials of indentations were carried out. The Vickers microhardness H_v of the crystal was evaluated using the relation $H_v = 1.8544\ (P/d^2) kg/mm^2$, where P is the indenter load in kg and d is the mean diagonal length of the impression in mm. The measurement was performed on the on the (001) plane of the SR and SEST-grown LAMD crystals. Improvement in the hardness behavior has been observed while measuring individual planes. The microhardness values vary with the method to grow crystals in the range (SEST) 12.4-32.3 kg/mm^2 and(SR) 15.2-36.7 kg/mm^2.The microhardness for single crystal of LAMD is determined as a function of load and variations of these values are provided in fig.The major contributions to hardness is

attributed to the high stress required for the homogenous nucleation of dislocation in the small dislocation free region indented .Hence higher hardness value for the SR method grown LAMD crystal indicated grater stress required for homogenous nucleation of dislocation in the small dislocation free region indented .Hence higher hardness value for the SR method grown LAMD crystal indicated greater stress required to form dislocation , which confirms greater crystalline perfection. The mechanical strength of the SR-grown LAMD crystal reveals that the crystal has a good hardness and it is useful for any applications. An increase in the mechanical strength will have significant effects on fabrication and processing such as ease in polishing and less wastage due to cracking/breakage while polishing.The high mechanical hardness contributes to attractiveness of the present compound in practical applications.

The SR-grown LAMD crystal has better crystalline perfection higher piezoelectric value, higher dielectric constant, lower dielectric loss, higher transparency and higher hardness than the SEST-grown LAMD crystals. These show that the quality of the SR-grown LAMD crystal is comparably higher than the conventional method grown LAMD crystals

SHG study

The SHG efficiency of LAMD is measured using the Kurtz-Perry powder technique. A fundamental wave with a pulse width of 8 ns, repetition frequency of 10 Hz, a beam diameter of 1 mm, energy of the laser pulse around 300 mJ and a wavelength of 1064 nm radiated from Nd:YAG laser source was focused on the samples using a lens with focal length of 120 mm . The grown single crystal of LAMD was powdered with a uniform particle size and densely filled into the quartz cell. A sample of potassium dihydrogen phosphate (KDP) , also powdered to the identical size as the experimental sample was used as a reference material in the SHG measurement. The transmitted fundamental wave was absorbed by a $CuSo_4$ solution and the second harmonic signal was detected by a photomultiplier tube and displayed on a storage oscilloscope. The generation of the second harmonics was confirmed by green radiation of 532nm in both conventional and SR method grown LAMD samples. The SHG conversion efficiency of both crystals grown from the SR method and SEST is found to be nearly 1.4 times greater than that of KDP.

Both crystals have the same SHG efficiency, since SHG is an intrisinic property of an NLO material. It does not depend on the preparation method of the matrial.In this

case , even the SR method grown crystal has better quality or more perfect than the crystal prepared by the conventional method; it was finally crushed into smaller grain size for the SHG measurement. The Kurtz and Perry method is a preliminary method. The SHG efficiency depends on the grain size of the powder sample and it also depends on the packing density of the sample in the capillary tube. Similar result has been reported in which the SHG efficiency of the SR and SEST-grown LAM crystals was 0.35 times than that of KDP.

Thermal analysis

Differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) of LAMD crystals were carried out in the temperature range of 0-500 ^{0} C in inert nitrogen atmosphere at a heating rate of 20 ^{0} C/min .The TGA and DTA curves of LAMD are shown in fig .4.The DTA curve of LAMD shows an endothermic peak at 95.8 ^{0} C , which can be attributed to the melting point of the sample. The compound starts to lose water at around 83.8 ^{0} C and continues up to 123.8 ^{0} C, in which 1/3 water molecule is eliminated at around the melting point. A second dissociation occurs at 182.5-217.5 ^{0} C , results in the formation of volatile substances probably carbon dioxide, ammonia and rest part of water molecule.Further heating does not produce any significant endothermic or exothermic peaks in the DTA curve, because DTA becomes inactive due to improper contact with the molten substance,whereas TGA shows complete weight loss. The studies revealed that the LAMD crystal is thermally stable up to 217.5 ^{0} C.

Conclusion

Bulk crystals of L-arginine maleate dihydrate was grown by solution growth method, in a period of two weeks. Using S-R Technique very large bulk transparent crystals were grown in a period of one month. The grown crystals were subjected to characterization studies such as XRD- to know the all parameters and structure, FTIR analysis for knowing the functional groups, Uv-vis NIR analysis, Microhardness studies, Dielectric measurement, Piezoelectric measurement, SHG conversion efficiency, Thermal studies.

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