Studies on growth, structural, optical, etching and nonlinear optical a properties of L–arginine maleate dihydrate single crystal for NLO application

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Abstract

Single crystal of L–arginine maleate dihydrate (LAMD) was grown by slow evaporation solution technique (SEST) at a constant temperature of 40°C. The crystallinity of grown single crystal was confirmed by powder X–ray diffraction (PXRD) analysis. The strain in the lattice of the material was calculated using Hall-Williamson co–efficient relation for the first time. It is evident from the optical absorption study that the grown crystal has less absorption in the entire visible region with a lower cut–off wavelength of 347 nm. Etching studies were carried out to analyze the surface properties of the grown LAMD crystal. The frequency conversion efficiency has been calculated using powder Kurtz and Perry technique.

Keywords: Single crystal; Solution growth; X-ray diffraction; UV-Vis NIR; Etching; SHG;

1. Introduction

Nonlinear optical materials are used for high–speed nonlinear optical applications such as electro-optics, optical parametric oscillation, second and third harmonic generation [1–2]. In literature some reports are already available on L–arginine maleate dihydrate nonlinear optical single crystal with the molecular formula of $C_{10}H_{22}N_4O_8$ with two water molecules [3]. In the present work few important analysis such as Hall–Williamson co–efficient with its structural and optical properties are reported for the first time. Also in the present work, LAMD single crystals were grown and subjected to various characterization techniques such as SHG and etching, and the results are discussed in detail in the forth-coming sections.

2. Experimental Procedure

L–arginine and maleic acid were taken in equimolar ratio and deionized water was used as solvent to synthesis LAMD. The saturated solution was prepared and filtered using Whatman filter paper to avoid residual solutes and impurities. The beaker was kept in a constant temperature bath (CTB) at 40° and recrystallization process was carried out twice inorder to improve the purity of LAMD crystal. After 20 days highly transparent single crystal with a dimension of 24×10×3 mm^3 was harvested.

3. Results and Discussion

3. 1. Powder X–ray diffraction analysis

Single crystals of LAMD was crushed into fine powder and subjected to powder X–ray diffractometer for phase analysis. The sharp peaks of PXRD pattern indicate the good crystallinity of the material. The lattice spacing ‘d’ was obtained from the ‘θ’ value for each peak. The strain (η) in the lattice of the grown crystal was evaluated using Hall–Williamson relation:

$$\beta \cos\theta = \frac{k\lambda}{\tau} + \eta \sin\theta \quad [1]$$

where β, θ, K, λ and τ are full width at half maximum, Bragg diffraction angle, Scherrer constant, wavelength of X–ray and crystallite size respectively. The value of the strain was measured from the slope drawn between β cos θ versus sin θ. The obtained curve was further linearly fitted to obtain strain value from the slope of linearity of data points. The slope value (η) obtained is 0.31 with an uncertainty of ± 0.09 that suggest the crystal carries compressive strain. It is worth to note here that the observed strain is due to point defects which give strain only around the defects core due to short-range order and thus the lattice parameters or unit cell volume of the material does not change [4]. The obtained powder X–ray diffraction pattern and hall-Williamson plot is shown in Fig. 1.

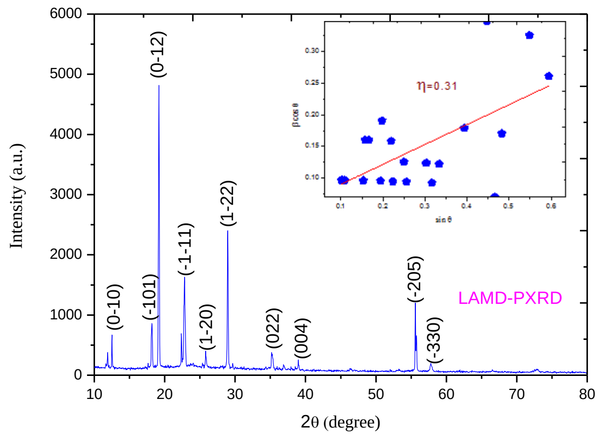

Fig. 1. Indexed PXRD pattern and Hall Williamson plot of LAMD

3. 2. UV–Vis NIR absorption study

UV–Vis NIR analysis is an important tool for NLO applications, because these materials can be used only if they have a wide transparency window. The absorption spectrum gives information about the structure of molecules, because the absorption of UV and visible light involves the promotion of electron in σ and π orbital from ground state to higher states. The lower cut–off wavelength of LAMD is found to be 347 nm, which is due to the excitation of electrons from the nonbonding to σ*. The band gap energy (E_g = 4.13 eV) of LAMD single crystal was evaluated by extrapolating a straight line part in the linear region of the graph at $(\alpha h\gamma)^2$=0. The low absorption of the material in the entire visible region is due to the delocalization of electronic cloud through charge transfer (CT) axis and this confirms its suitability for nonlinear and other optoelectronic applications. The recorded optical absorption spectrum and the Tauc's plot for LAMD drawn as $(\alpha h\gamma)^2$ versus hγ is shown in **Fig. 2.**

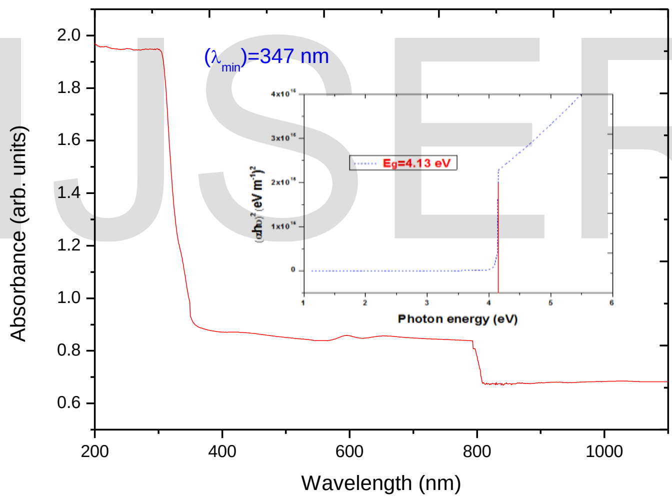

Fig. 2. UV Vis NIR spectrum and Eg analysis of LAMD

3. 3. Chemical etching analysis

Surface morphological study is a revolutionary technique to reveal the lattice defects and crystal symmetry on the surface of the grown single crystals. The grown LAMD single crystal with good quality was selected prior to perform the etching studies inorder to ensure the growth pattern, defects, hillocks and morphology. The sample was chemically etched using water as etchant. In the process of chemical etching, etching time, concentration of etchant (etchant ratio) and selective etchant play vital roles. The etchant was selected based on their dissolution properties and the etching duration was fixed as 5 s. The crystal was dipped into the etchant and wiped with a tissue paper. The corresponding crystal surfaces were analyzed using an optical microscope in the reflection mode. The etched surfaces of the crystal are shown in **Fig. 3** and it was found that the surface of the crystal before etching was smooth. As the etching time is increased from 5 s to 20 s, bunched parallel layers were observed on the surface of the material, which are called growth striations. Randomly distributed, but strictly oriented etch pits have been seen and the number of etch pits are less. This may be due to the adsorption of impurity and growth fluctuations during supersaturation. The calculated etch pit density of LAMD is 1.27×10^{2} cm^{-1}.

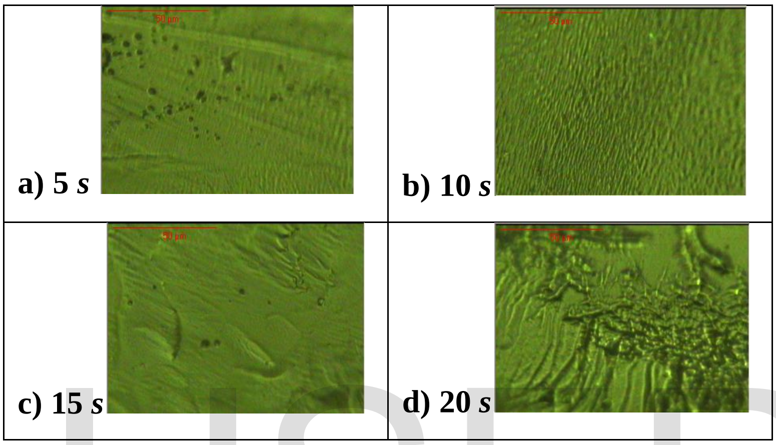

Fig. 4. Micrographs for the surface of LAMD single crystal during etching

3. 4. SHG test

The powder Kurtz and Perry technique is the first and widely used technique for confirming the frequency conversion efficiency of SHG materials [5]. A Q–switched mode–locked Nd: YAG laser source of pulse width 8 ns at a wavelength of 1064 nm and 10 Hz fundamental radiation was illuminated on the microcrystalline powder sample of LAMD. The input laser pulse energy of 1.2 mJ beam was directed through an IR reflector and made to incident on the microcrystalline powdered sample packed in a capillary tube with a diameter 0.154 mm. A detector and oscilloscope assembly were used to measure the emitted light passed through the IR filter. The second harmonic signal (532 nm) of 4.0 mV was recorded as the output. The frequency conversion efficiency of LAMD crystal is calculated by comparing with the microcrystalline powder of KDP after the measurements. The frequency conversion efficiency of LAMD is 0.6 times that of standard KDP as a reference material and also it is closer to the value reported by V. Revathi et. al [6].

4. Conclusion

The grown crystals were subjected to powder X–ray diffraction analysis and the calculated strain values. Optical absorption study shows that the absorbance value is found to be very low that confirms its suitability for linear and nonlinear optical applications. Etching studies were performed on the grown single crystal for analyzing the surface properties of grown LAMD. The SHG efficiency of LAMD is observed as 60% to that of standard KDP.

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