Vickers micro hardness and etching studies of L-arginine semi-oxalate single crystal for optoelectronic applications

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L-arginine semi-oxalate (LASO) single crystals were grown by slow evaporation method. The crystal crystallizes in triclinic structure with P1 symmetry and the unit cell parameters of grown crystals were evaluated by single crystal X-ray diffractometer to confirm the triclinic structure of the crystal. The investigation on the mechanical property was carried out using Vickers micro hardness tester. Etch pattern of hillocks were observed on the surface of grown crystal due to reactions of the etchant with dislocations sites. Second harmonic generation studies were performed by Kurtz and Perry method to confirm the nonlinearity of the grown crystal. These preliminary investigations suggest that the present compound L-arginine semi-oxalate (LASO) single crystals can serve as a potential candidate for optoelectronic applications.

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1. Introduction

The research for nonlinear optical (NLO) materials finds considerable interest among the scientists due to their essential impact on laser technology, fiber optic communication, optical modulation and optical data storage technology [1-3]. To identify novel crystals of NLO properties, we have grown L-arginine semi-oxalate (LASO) crystals by slow evaporation technique at room temperature. L-arginine semi-oxalate crystal is one of the organic materials possessing the characteristics of organic moiety due to weak van der Waals forces and hydrogen bonding which lead to high degree of electronic charge distribution leading to a high mobility of the electron density [4, 5]. Functionality of both ends of the π bond system with appropriate electron donor and acceptor groups can enhance the asymmetric electronic distribution in either or both ground and excited states, leading to an increased optical nonlinearity. From the literature survey, there were reports presented earlier on the crystal structure whereas the other etching and hardness studies were not reported till date. For any optical device fabrications, the crystals should possess wide transparency and moderate mechanical strength to withstand the thermal shock and high temperature generated due to laser heating. Hence, considering the above aspects, the present work is focused on the hardness and surface morphology of the grown LASO crystals. Vickers micro hardness and Etching studies of LASO crystals have been carried out and the results are discussed in detail.

2. Experimental details

2.1. Synthesis of LASO crystal

L-arginine semi-oxalate single crystal was grown from aqueous solution containing L-arginine (Loba chemie-99%) and oxalic acid dihydrate (Loba chemie-99%) in molar ratio 1:1 at room temperature. Calculated amount of reactants were dissolved in double distilled water and stirred well by using magnetic stirrer to ensure homogeneousness of the solution. The solution was then filtered using filter paper and transferred to a Petri dish. The prepared solution was allowed to evaporate at room temperature. The growth was initiated following the nucleation due to slow evaporation of the mother solvent. After a period of 45 days, the crystals were harvested. The quality of the grown crystal was improved by repeated crystallization process. The gown crystals were found to be colourless and non-prismatic with more transparency. Fig. 1 shows the photograph of the as-grown crystal with scale (10 × 9 × 2 mm^3). The growth data of the grown LASO single crystals are given in Table 1.

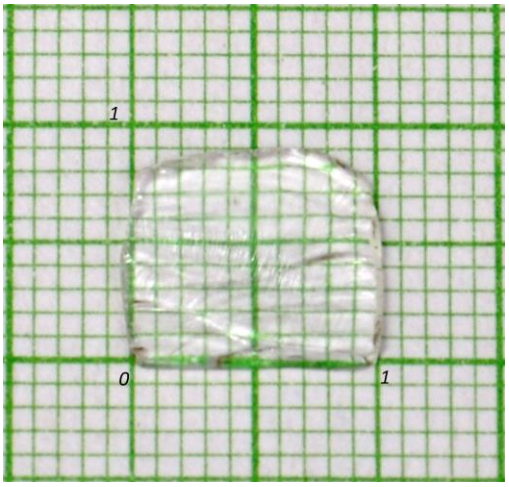

Fig. 1. Photograph of the as-grown crystal LASO

Table 1. Growth data of LASO single crystal

Method of Growth	Slow evaporation Technique
Solvent used	Deionized water (H_2O)
Molar ratio (L-Arginine: Oxalic acid)	1:1
Temperature for growth	Room Temperature (35° C)
Period of growth	45 days (Nucleation from seed crystals)
Dimensions of the as grown crystal	10 × 9 × 2 mm^3

2.2. Characterization studies

The grown crystal was subjected to various characterization techniques to assess its structural, surface features and hardness. Single crystal X-ray diffraction studies of the grown crystal LASO were carried out at 293° C using Bruker Kappa APE XII single crystal X-ray diffractometer fitted with MoKα (λ=0.71069 Å) radiation. REICHERT MD 4000E ULTRA micro hardness tester with diamond pyramid indenter attached to an optical microscope was used to analyze the mechanical property. Etching studies were analyzed using RICHERT POLYVAR 2 MET photomicroscope with magnification 80× and water was used as etchant. Nonlinear property of LASO crystals was confirmed by Kurtz and Perry powder technique using Q-switched high energy Nd:YAG laser (QUANTA RAY model LAB-170-10).

3. Results and discussion

3.1. Single crystal X-ray diffraction analysis

The grown crystal was used to measure the intensity data and θ value was varied from 2.55° to 25°. The structure of the crystal was solved by direct method procedure using the SIR-92 (WINGX) computer program. The structure was refined by the full matrix least square using SHELXL-97(WINGX) program. During the course of data collection, one standard reflection was monitored for every 100 reflections without significant variation.

This study reveals that the grown LASO crystal possesses triclinic structure with non-centrosymmetric space group, P_1. The lattice parameters were measured as a = 5.05 Å, b = 9.73 Å, c =13.12 Å; α = 111.03°, β = 92.79° and γ = 91.91° and unit cell volume V= 600 $Å^3$. These results are found to be in good agreement with the earlier reported values [6, 7].

3.2. Vickers micro hardness test

Good quality crystals with excellent optical properties and mechanical behaviour are required for device applications. Vickers micro hardness testing is a versatile technique to analyze the mechanical strength of the grown crystal [8]. For the accuracy of the results, several indentations were made on the sample with a dwell time of 5 seconds. The Vickers hardness number (Hv) was calculated using the standard formula [9-11]

$$H_v = 1.8544\ P/d^2\ kg/mm^2$$

where P is the applied load and d is the mean diagonal length of the indentation. The plot of applied load against hardness is shown in Fig. 2. It reveals that hardness of grown crystals increases with load and attains maximum for the load of 30g. On further increasing the load, the hardness value is found to decrease very steeply. The sudden dip in the curve is due to the loosely packed lattice with reduced bond energy or interlocking of microstructures at higher loads [12]. The increasing trend of micro hardness with the load up to 30g indicates that greater stress is required to form slip dislocation. The material can withstand maximum stress up to a load of 30g during the process of fabrication.

The Mayer's index number was calculated by using Mayer's law, which relates the load and the indentation diagonal length as

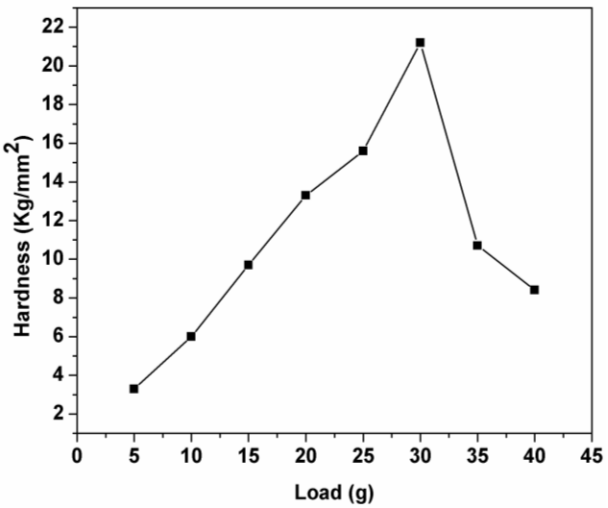

Fig. 2. Variation of hardness with load for LASO crystal

$$P = k\ d^n$$

where *n* is called Mayer's index or work hardening index. In order to find work hardening index (n), a plot of log P against log *d* was drawn as shown in Fig. 3. From the slope of the straight line, the Mayer's index number was found to be 3.75. According to Onitsch, if *n* is greater than 2, the micro hardness will increase with the increase of load [13, 14]. The Onitsch condition will provide information about the increase or decrease of hardness value with load. The Onitsch condition cannot be used to explain the peak in the plot. Since *n* value is greater than 2, the material is found to possess soft nature [15, 16].

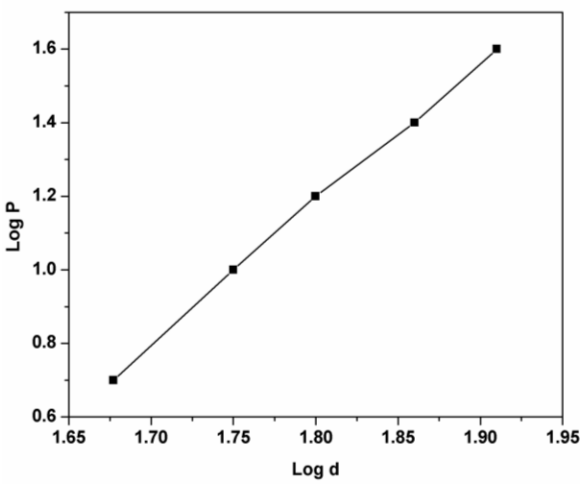

Fig. 3. Plot of log d vs log P for LASO crystal

3.3. Etching studies

Etching study is very useful to analyze the dislocations and growth mechanism. The grown crystal is highly soluble in water. Therefore, water was chosen as etchant.

The crystal with more transparency was selected for etching study. The surface of the crystal was first etched using distilled water for 15 sec at room temperature. The Etch pattern was photographed using photomicroscope [17]. Microphotograph of crystal before etching is shown in Fig. 4 (a). Before etching, the surface of the crystal is found to contain blemishes. After etching, Bizzare shaped elevations and hillocks were observed as shown in the Fig. 4 (b). Image J software was used to identify the shape of etch pattern. The height of hillocks was roughly was measured as 400 Å using the above software [18]. Etch pattern is due to the reactions of the etchant with dislocation sites. The shape and size of the etch pattern will change depending upon the type of etchant and at the time of etching.

When the surface of the crystal was etched with water for 30 sec, the size of each etch pit was reduced as shown in Fig. 4 (c). This is due to the removal of certain atoms from the surface and also due to the orientation of the surface. It is clearly understood that the etch pit formation is due to reaction of the etchant with dislocation sites present on the surface of grown crystal. The dislocation density can also be calculated by counting the etch pits around a particular area. These dislocations provide the necessary steps required for the growth of crystal. Hence, etching study can analyze the presence of dislocations and dislocation density. From the knowledge of dislocation density, we can interpret the magnitude of dislocations present in the grown crystal [19].

Fig. 4.(a) Etch pattern of LASO before etching

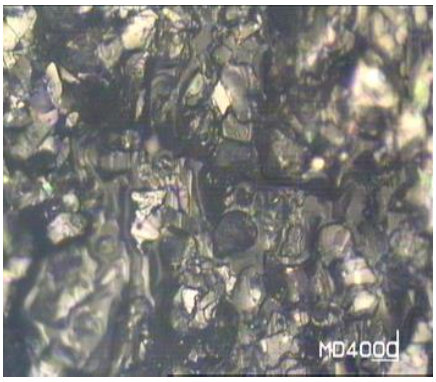

Fig. 4.(b) Etch pattern of LASO after etching for 15 sec

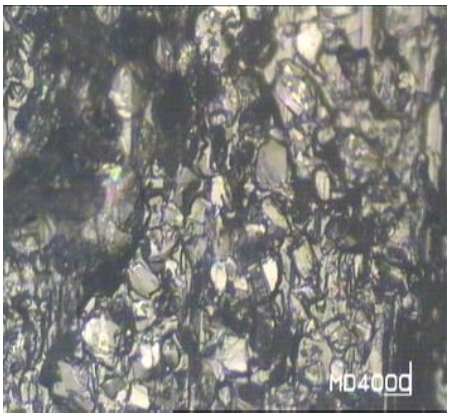

Fig. 4.(c) Etch pattern of LASO after etching for 30 sec

3.4. Second harmonic generation

Nonlinear property of LASO crystals was confirmed by Kurtz and Perry powder technique [20]. The grown crystal of LASO was crushed to fine powder and placed in a microcapillary of uniform bore. A high intensity laser radiation was passed through the sample packed in a capillary tube of diameter 0.154mm. When a laser input of 0.68 J was passed through LASO crystal, second harmonic signal of 13.2 mJ was produced. The output of LASO was compared with that of KDP (8.8mJ). Hence, the SHG efficiency of LASO crystal is found to be 1.5 times that of KDP [21].

Since the grown crystal belongs to non-centrosymmetric space group, the second order susceptibility is not equal to zero. In the case of centrosymmetric crystals the second order susceptibility is zero. Therefore, the grown crystal can induce polarization due to non-centrosymmetric nature to exhibit second order harmonics. The grown crystal LASO is of zwitterionic nature due to non-centrosymmetric space group for the material to reveal NLO property. This is the mechanism behind Second Harmonic Generation. Moreover SHG efficiency of the material depends upon the size of the powder sample. The efficiency will be improved if the size of the sample powder is reduced. In the present work, the sample is taken in the form of fine powder for obtaining better SHG efficiency.

4. Conclusions

Transparent single crystals of L-arginine semi-oxalate (LASO) were successfully grown by slow evaporation technique. From the single crystal XRD data, it is observed that the grown crystal belongs to triclinic structure with non-centrosymmetric space group P_1. Vickers micro hardness studies reveal that the grown crystal possesses good mechanical strength which is the prime requirement for optical crystals in device fabrication. Etching studies strongly suggest that the growth mechanism is based on surface diffusion theory due to the presence of dislocations. Second harmonic generation (SHG) efficiency was found to be more than that of standard KDP single crystals. Hence, the grown single crystal LASO is found to be a potential candidate for applications in optoelectronic devices.

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References

[1] L. Misogutti, A. T. Verala, F. D. Nunes, V. S. Baganato, F. E. A Melo, J. Mendes Filho, S. C. Zillio, Opt. Mater. **6**, 147 (1996).

[2] P. N. Prasad, D. J. Williams, John Willey & Sons Inc., New York, USA, 1991.

[3] H. S. Nalwa, M. Seizo, "Nonlinear Optics of Organic Molecules and Polymers", CRC Press, New York, USA, 1997.

[4] S. B. Monaco, L. E. Devis, S. P. Velsko, F. Wang, D. Elimerl, A. Zalkin, J. Cryst. Growth **85**, 252 (1987).

[5] A. M. Petrosyn, R. P. Sukiasyan, H. A. Karapetyan, S. S. Terzyan, S. S. Figelson, J. Cryst. Growth **213**, 103 (2000).

[6] N. R. Chandra, M. M. Prabu, J. Venkataraman, S. Suresh, M. Vijayan, Acta Crystallogr. Sect. B **54**, 257 (1998).

[7] P. Vasudevan, S. Gokul Raj, S. Sankar, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy **106**, 210 (2013).

[8] W. Mott, "Micro Indentation Hardness Testing", butterworths, London, 1956.

[9] E. Chacko, J. Mary linet, S. Mary Navis Priya, C. Vesta, B. Milton Boaz, Jerome Das, J. Pure. Appl. Phys. **44**, 260 (2006).

[10] K. D. Parikh, D. J. Dave, B. B. Parekh, J. Joshi, J. Adv. Mater. **5**, 1 (2016).

[11] Keshra Sangwal, Barbara Surowska, Mater. Res. Innovat. **7**, 91 (2003).

[12] B. S. Shah, Cryst. Res. & Technol. **17**, 27 (1982).

[13] S. Boomadevi, H. P. Mittal, R. J. Dhanasekaran, J. Cryst. Growth **261**, 55 (2004).

[14] Dipak J. Dave, Ketan D. Parikh, Mihir J. Joshi, Adv. Mater. Res. **665**, 172 (2013).

[15] S. Karan, S. P. S. Gupta, Mater. Sci. Eng. **398**, 198 (2005).

[16] G. Ramesh Kumar, S. Gokul Raj, Advances in Materials Science and Engineering **2009**, Article ID 704294, 40 pages.

[17] Sangwal (ed), Etching of Crystals, North-Holland Physics Publishing, The Netharlands, 1987.

[18] Hideho Saito, John Borland, Hajime Asahi, Haruo Nagai, Kiyoshi Nawata, J. Cryst. Growth **64**, 521 (1983).

[19] K. D. Parikh, D. J. Dave, M. J. Joshi, B. B. Parekh, Int. J. Chemical Concepts **2**, 50 (2016).

[20] S. K. Kurtz, T. T. Perry, J. Appl. Phys. **39**, 3798 (1968).

[21] V. Siva Shankar, R. Sankar, R. Siddheshwaran, R. Jayavel, P. Murugakoothan, Mater. Chem. Phys. **109**, 119 (2008).

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