Mechanical, Electrical and Etching Study of Potassium Iodide Doped L-Threonine Single Crystal

WANKHADE PRATIK, M, PAHURKAR VIKAS G., MULEY GAJANAN G.

Department of Physics, Sant Gadge Baba Amravati University, Amravati, Maharashtra, India
E-mail: pwyashpm8@yahoo.com

Abstract

Amino acid based organic single crystal of potassium iodide doped L-threonine (LTPI) was grown by low temperature solution growth method from aqueous solution. In the present study, the grown nonlinear optical (NLO) single crystal LTPI has been subjected to the Vickers hardness, electrical and etching studies to decide its possible use in NLO applications. Vickers hardness study was carried out with variation in indentation time at a constant applied load. Elastic stiffness constant has been calculated from hardness number. The variation of ac resistivity with frequency has been presented. ac resistivity gradually decreases with increase in frequency at a room temperature. Electrical activation energy is also calculated. Etching study reveals growth of the crystal takes place by 2D nucleation mechanism.

Key words: Single crystal, Vickers hardness, Electrical properties**,** Etching study

Introduction

Second harmonic generation, third harmonic generation, other frequency conversion processes, and optical rectifications are the key nonlinear optical (NLO) processes. These processes find applications in science and technology such as optical modulation, optical switching, optical rectification, optical communication, device fabrication, etc [1-3]. These applications depend upon the knowledge of material properties, such as optical transparency, birefringence, thermal, electrical and mechanical hardness [4]. Now days, amino acids based nonlinear optical single crystal have been studied in large scale for possible NLO applications. In this regards a number of amino acid based single crystal have been reported so far [4-6]. Amino acid based single crystal material is classified into three categories depends on the type of bonding between the atoms in the molecule. Out of which organic material has been well attracted the attention of scientific society. Since organic materials show good physiochemical properties like easy for synthesis, good second harmonic generation efficiency, extremely good mechanical and thermal properties, readily soluble in aqueous and organic solvents [7-8]. Potassium iodide doped L-threonine (LTPI) is one of the recently reported organic NLO crystal from our laboratory. The details regarding the growth, spectroscopic, second harmonic generation, thermal and optical study was reported elsewhere [9]. In this article, details regarding the crystalline structure, micro-hardness, electrical and etching study are reported.

Synthesis and crystal growth

Amino acid L-threonine and Potassium iodide both (AR grade, S D Fine-Chem. Ltd. India) were used as it is to grow potassium iodide doped L-threonine crystal. L-threonine and potassium iodide were taken in equimolar molar ratio and dissolved in double distilled water, stirred continuously for four hours to prepare homogeneous solution and filtered using membrane filter. The solution was kept in constant temperature water bath at 40^{o}C, for spontaneous crystallization to crystallize the title compound. The synthesized compound was crystallized within 8-9 days. The crystalline sample was washed with double distilled water and re-dissolved in it, stirred, filtered and kept at 35^{o}C constant temperature for spontaneous crystallization to get seed crystals. Good quality seed crystal was harvested within 3-4 days. The seed crystal was used to grow big size crystal. Good quality single crystal of size 28x9x7mm^3 was grown within 17 days by slow solvent evaporation of aqueous solution at constant temperature 35^{o}C.The photograph of the grown big size crystal is as shown in fig1.

Fig1.Photograph of LTPI single crystal

Result and Discussion

Single crystal XRD: Single crystal XRD pattern of the LTPI crystal is present in table1.LTPI crystallizes in the same crystal system and space group as that of pure L-threonine single crystal. There are observed, some slight changes in the lattice parameters, which may be due to the inclusion of potassium and iodine atoms in the pure crystal. The presence of potassium and iodine may influence their surrounding and distort lattice locally, which leads to the change in lattice parameters of the parent crystal [7,9,10].

Table1: Lattice parameter of LTPI single crystal

Single crystal XRD	Symmetry and space group	Lattice parameters (Å)		
		a	b	c
LTPI	Orthorhombic $P2_12_12_1$	5.125	7.690	13.52
Pure L-Threonine	Orthorhombic $P2_12_12_1$	13.611	7.738	5.144

Vicker's hardness test

Study of mechanical strength of the material crystal is the important parameter from device fabrication point of view. Mechanical hardness is the opposition to the plastic deformation under an applied load offered by a material. 11.The Vicker's microhardness study was carried out on the flat surface of crystals using FUTURE TECH MICROHARDNESS TESTER FM-700 fitted with diamond indenter attached to an optical microscope. The LTPI crystal surface (1 0 0) is polished and lapped before recording the hardness value. The variation in dwell time for same load was done. Each time the cracks were initiated on the crystal surface around the indentation for the constant applied load 5 gram. The observed micro hardness number (Hv) was tabulated in the table2. It is noted that hardness value increases with increase of dwell time. The observation reveals that, single crystal has large ability of the material to sustain the load for larger period of time without releasing internal energy.

Elastic stiffness constant give the broad idea about the tightening of the bonds between adjacent atoms. It has been estimated from Wooster's empirical relation 12 C11=HV7/4.

Table 2**:** Micro hardness number (Hv**)** and Elastic stiffness constant of LTPI single crystal

Dwell time(S)	**5**	10	15
Hv (Kg/mm^2)	90.5	94.5	104.7
$C11\times10^{14}$(Pa)	26.55	28.64	34.26

The increase in the hardness number can be attributed to the electrostatic attraction between the zwitterions present in the molecule. The zwitterions nature of the molecule favors for good mechanical strength of amino acids crystal [13]. For the higher loads cracks were observed on the surface. It may be due to the release of internal stress generated locally by the indentation [14].

ac Resistivity : The variation in ac resistivity versus log of frequency for the LTPI crystals is shown in fig 3. The ac resistivity was calculated using the following formula:

$$\sigma_{ac} = \frac{2\pi fCt}{A} \qquad \ldots (3) \qquad \sigma_{ac}=1/\rho_{ac},$$

Where C is the capacitance, t is the thickness, A is the area of the crystal, and f is the frequency of the applied field [15]. As shown in Fig. 3, ac resistivity decreases with the applied frequency across the grown crystal.

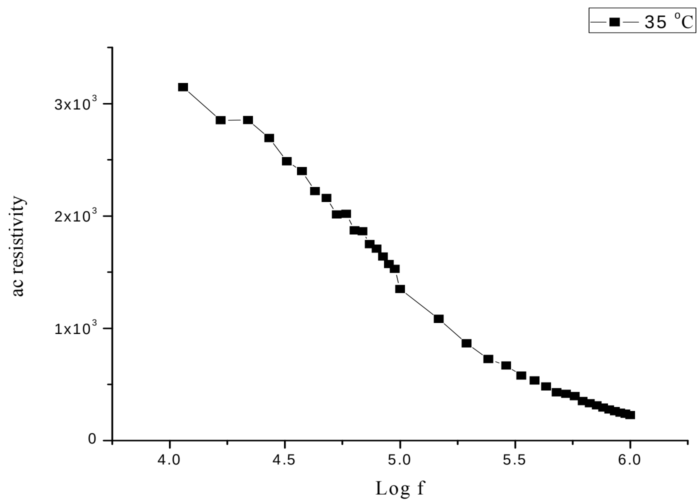


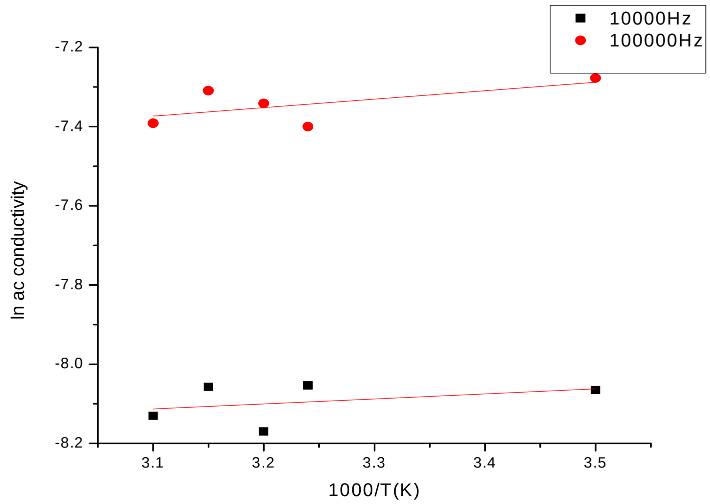
Fig.3: ac resistivity Vs log frequency for LTPI single crystal.

Activation energy

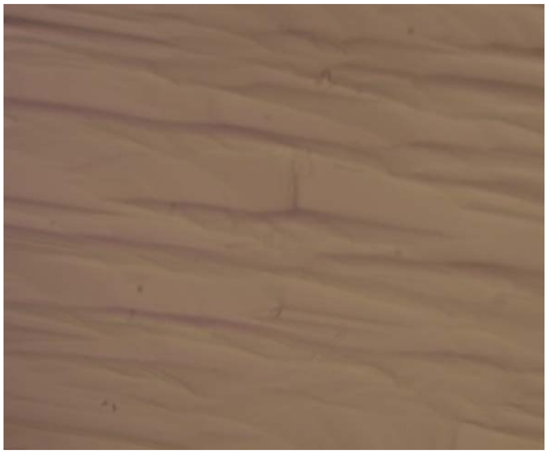
The graph plotted in between ln σ_{ac} and 1000/ T (k) was found to be linear nearly. So, the conductivity values can be fitted to the relation $\sigma_{ac} = \sigma_0 \exp[-E/(kT)]$, where E is the activation energy, k the Boltzmann constant(1.38×10^{-23}J /k), T was the absolute temperature and σ_0 the parameter depending on the material. Activation energies were estimated using the slope of the plot of above line [$E = -$ (slope) $k \times 1000$][16].The low activation energies confirm that the trapping levels originating probably from the defect states that are responsible for conduction in the region.

Table 3: Activation energy for LTPI single crystal.

Sr. No	Name of sample	Slope		Activation energy(eV)	
		10^4Hz	10^5 Hz	10^4Hz	10^5 Hz
1	LTPI	0.126	0.213	-1.08×10^{-2}	-1.83×10^{-2}



Etching study



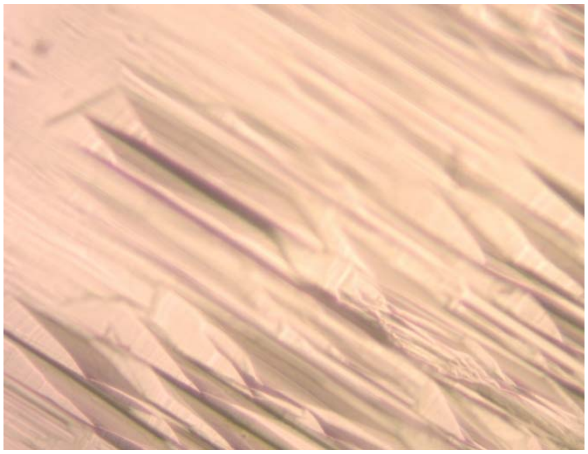


Fig 4(a): LTPI without etching Fig 4(b): LTPI with etching

The physical properties of the crystal were known for possible NLO applications. The physical properties may be conductivity, hardness, dielectric etc. All these properties depend on the crystal quality. The crystal quality depends on the presence of dislocations. The dislocation was produced at the time of growth. Etching studies fetch the knowledge of crystal growth mechanism. For that, it has to be done. Etching was carried out on the grown crystal of LTPI. The shape of the etch pits depends on the lattice structure and symmetry of the crystal[17].The surface of the crystal was clean and photograph of the surface has taken with the help of AXION MICROSCOPE connected to the computer. Fig 4. (a) Shows the rectangular elongated with ended etch pit. Then the crystal was immersed in double distilled water for 5s.The crystal was clean and dried with soak paper and again observed under the optical microscope. The observed photograph was as shown in fig4. (b).From the fig4. (b), the same rectangular ended elongated etch pits and striation was observed. The rectangular etch pit confirm the growth of the crystal from 2D nucleation mechanism. The etch pits does not disappear upon etching indicate the presence of dislocations [18].

Conclusion

Single XRD study confirms crystal belongs to orthorhombic crystal structure. There is increasing in hardness number with dwell time confirms single crystal sustains the load for larger period of time without releasing internal energy. Elastic stiffness constant indicates bond tightening of the material is good. Etching study observed rectangular ended elongated and striations etch pit. Etching study confirms the growth of the crystal from 2D nucleation mechanism and presence of dislocations in the crystals.

Acknowledgement

The authors acknowledge the support of Dr. R. K. Goyal (Department of metallurgy and material science, college of engineering, Pune, India) for Hardness measurement.

References

1 G. Ramesh Kumar, S. Gokul Raj, R. Mohan, R. Jayavel, J. Cryst. Growth, 2005, 267, 213-217.
2 J. J. Rodrigues Jr., L. Misoguti, F. D. Nunes, C. R. Mendon, S. C. Zilio, Opt. Mater., 2003, 22, 235-240.
3 G.Anbazhagan, S.Joseph, Shankar, Opt.Comm.,2013, 291,304-308.
4 Redrothu Hanumantha Rao , S. Kalainathan, Mater. Res. Bull., 2012, 47, 987-992.
5 M. Lydia Caroline, R. Sankar, R.M. Indirani, S. Vasudevan , Mater. Chem. and Phys. 2009,114, 490-494.
6 M. Narayan Bhat, S. Dharmaprakash, J. Cryst. Growth 2002,236, 376–380.
7 T. Pal, T. Kar, G. Bocelli, L. Rigi, J. Cryst. Growth and Des. , 2003,3, 13-16.
8 R. Hanumantharao , S. Kalainathan, Spectrochim. Acta Part A: Mol. Biomol. Spectro., 2012, 94,74-83.
9 P.M.Wankhade, G.G.Muley, J. of nonlinear opt. Phys. and Mater., 2013,22, 3,
10 D. P. Shoemaker, J. Donohue, V. Schomaker ,R. B. Corey, J. Am. Chem. Soc. 1950, 72, 2328–2349.
11 K. Seethalakshmi , S. Perumal, P.Selvarajan. World J. of Sci. and Techno. 2012, 2, 7,124-127.
12 M. N. Ravishankar,R. Chandramani, J. Optoelectron. and Biomed. Mater. 2011, 3,101-106.
13 Reena Ittyachan, Preema C. Thomas, D. Prem Anand, M.Palanichamy, P. Sagayaraj, Mater. Chem. and Phys. 2005,93, 272–276.
14. S. Arjunan, Bhaskaran, Mohan kumar, Mohan, Jayavel, J. of alloys and comp. 2010, 506,784–787

15 N. Kanagathara and G. Anbalagan , Inter. J. Opt., 2012, 2012, ,.

16. A anne assencia and c mahadevan, , Bull. Mater. Sci., 2005, 28, 5, 415–418.

17. K. Sangwal and I. Owczarek, , J. of Cryst. Growth, 1993,129, 3-4, 640-652.

18. S.Supriya S.Kalainathan, Asian J.biochem. pharm. Res.,201, 2,1, 640-649.