OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 4, No. 11, November 2010, p. 1743 - 1746

Mechanical and dielectric studies of L-Prolinium Tartrate (LPT) NLO single crystals

S. SURESH*, A. RAMANAND, D. JAYARAMAN[a], P. MANI[b]
Department of Physics, Loyola College, Chennai-600 034, India
[a]*Department of Physics, Loyola Institute of Technology, Chennai-602 103, India*
[b]*Department of Physics, Hindustan University, Padur, India*

L-Prolinium Tartrate (LPT) crystals are capable of generating second harmonics, a unique property which can be used for device fabrication in opto-electronics. Single crystals of L-Prolinium tartrate $(C_5H_{10}NO_2)^+(C_4H_5O_6)^-$, were grown from aqueous solution by slow evaporation technique. Single crystal X-ray diffraction analysis shows that the crystal belongs to monoclinic system with the space group P21. Several solid state physical parameters have been determined for the grown crystals. The anisotropy in Vicker's micro hardness leads to the study of various parameters such as fracture toughness (K_c), brittleness index (B) and yield strength (σ_v). The dielectric constant and the dielectric loss of the grown crystal were studied as a function of frequency and temperature.

(Received September 8, 2010; accepted November 10, 2010)

Keywords: Single crystal, Growth from solution, X-ray diffraction, Vicker's microhardness tester, Dielectric constant

1. Introduction

Extensive studies have been made on the synthesis and crystal growth of nonlinear optical (NLO) materials over the past decade because of their potential applications in the field of telecommunications, optical signal processing, and optical switching. Organic materials have been of particular interest because the NLO response in this broad class of materials is microscopic in origin, offering an opportunity to use theoretical modeling coupled with synthetic flexibility to design and produce novel materials [1, 2]. In solid state, amino acid contains the donor and acceptor groups, which provide the ground state charge asymmetry of the molecule, required for second-order nonlinearity [3–7]. Proline is an abundant amino acid in collagen and is exceptional among the amino acids because it is the only one in which the amine group is part of a pyrrolidine ring, making it rigid and directional in biological systems [8]. Single crystal of L-proline shows no center of symmetry and its NLO coefficients have been examined by Boomadevi et al. [9]. Martin Britto Dhas et al. [10] have reported that the second harmonic generation (SHG) efficiency of L-prolinium tartrate is90% of that of standard potassium dihydrogen orthophosphate (KDP) crystals. Growth and characterization of L-Proline tartrate single crystals by slow evaporation and slow cooling technique has been reported [11]. In the present study, growth has been carried out by using slow evaporation technique method [11] and some physical parameters such as valance electron plasma energy, Penn gap, Fermi energy and electronic polarisability have been obtained for L-Proline tartrate single crystal. Vicker's indentation test enumerating the mechanical strength of the crystal has been determined, and the fracture toughness, brittleness index and yield strength for the grown crystal have been estimated. The dielectric constant and the dielectric loss have been determined as a function of frequency and temperature for the L-Prolinium tartrate single crystal.

2. Crystal growth

Single crystals of LPT $[(C_5H_{10}NO_2) + (C_4H_5O_6)^-]$ were grown from L-Proline and L-Tartaric acid taken in the equimolar ratio in aqueous solution by slow evaporation method. The solution was stirred continuously using magnetic stirrer for 3 days. The prepared solution was filtered and kept undisturbed at room temperature. Tiny seed crystals with good transparency were obtained due to the spontaneous nucleation. Among them, defect free seed crystal was suspended in the mother solution, which was allowed to evaporate at room temperature. Large size single crystals were obtained due to collection of monomers at the seed crystal sites from the mother solution. Fig. 1 shows as grown crystals of LPT.

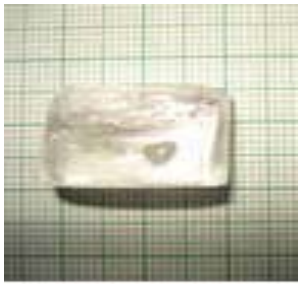

Fig. 1. Photograph of single crystals of LPT.

3. Single crystal X-ray diffraction

Single crystal X-ray diffraction analysis for the grown crystals has been carried out to identify the cell parameters using an ENRAF NONIUS CAD 4 automatic X-ray diffractometer**.** Calculated lattice parameters are: a = 5.0013 Å, b = 17.6874 Å, c = 6.5268 Å, β = 100.45°and the space group is P_{21}. These values are found to agree with the reported values [11].

4. Some characteristic data

The crystals obtained are nonhygroscopic in nature and exhibit orthorhombic morphological forms. The valence electron plasma energy, $\hbar\omega_p$ is given by

$$\hbar\omega_p = 28.8(Z\rho / M)^{1/2} \tag{1}$$

where Z = ((9 x Z_C) + (9 x Z_H) + (1 x Z_N)) = 50 is the total number of valence electrons, ρ is the density and M is the molecular weight of the L-Proline tartrate single crystal. The Plasma energy is terms of Penn gap and Fermi energy [12] as,

$$E_P = \frac{\hbar\omega_P}{(\varepsilon_\infty - 1)^{1/2}} \tag{2}$$

and

$$E_F = 0.2948\left(\hbar\omega_p\right)^{4/3} \tag{3}$$

Polarizability, α is obtained using the relation [13]

$$\alpha = \left[\frac{(\hbar\omega_p)^2 S_0}{(\hbar\omega_p)^2 S_0 + 3E_p^2}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} cm^3 \tag{4}$$

where S_0 is a constant for a particular material, and is given by

$$S_0 = 1 - \left[\frac{E_F}{4E_F}\right] + \frac{1}{3}\left[\frac{E_F}{4E_F}\right]^2 \tag{5}$$

The value of α so obtained agrees well with that of Clausius-Mossotti equation, which is given by,

$$\alpha = \frac{3M}{4\pi N_a \rho}\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} \tag{6}$$

All these calculated data for the grown crystal are shown in the Table 1.

Table 1. Some theoretical data for LPT single crystal.

Parameters	Values
Plasma energy (eV)	22.39
Penn gab (eV)	1.923
Fermi gap (eV)	18.58
Polarizability (cm^3) Penn analysis	6.662 x 10^{-23}
Clausius-Mossotti Equation	6.677 x 10^{-23}

5. Mechanical property

Micro hardness studies of any system has a direct correlation with the crystal structure and is very sensitive to the presence of any other phase or phase transition and lattice perfections prevalent in the system. The hardness of the material depends on the different parameters such as lattice energy, Debye temperature, heat of formation and interatomic spacing. The hardness tests for LPT crystal was carried out by Leitz micro hardness tester with a diamond pyramidal indenter. The diagonal length of the indentation for various applied loads in kg is measured for a constant indentation period of 15 sec. The Vickers' hardness number (H_v) is calculated using the relation

$$H_V = \frac{1.8544P}{d^2} kg / mm^2 \tag{7}$$

where P is the applied load in kg and d is the diagonal length in m. The variation of Hv with the applied load P is shown in Fig. 2 and a plot of log P versus log d for the grown crystal is shown in Fig. 3. The plot between log P versus log d yields a straight line graph and its slope gives the work hardening index n, and is found to be 1.93. According to Meyer's relation

$$P = K_1 d^n \tag{8}$$

where K_1 is the standard hardness value which can be found out from the plot of P versus d^n. Since the material takes some time to revert to the elastic mode after every indentation, a correction x is applied to the d value and the Kick's law is related as

$$P = K_2\left(d + x\right)^2 \tag{9}$$

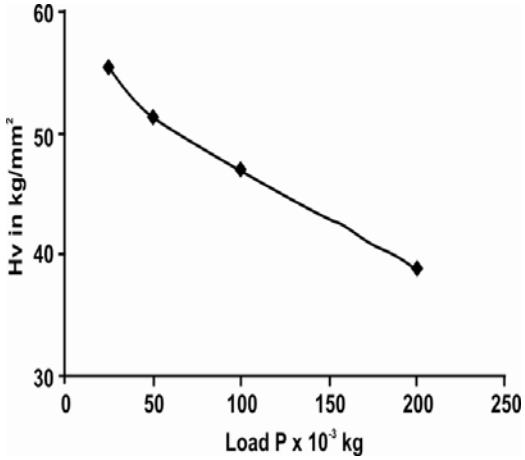

Fig. 2. Hv versus load P.

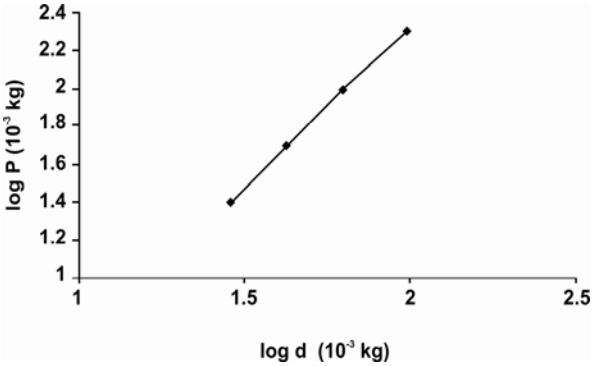

Fig. 3. log P versus log d.

From Eqs. (10) and (11)

$$d^{n/2} = \left(\frac{K_2}{K_1}\right)^{1/2} d + \left(\frac{K_2}{K_1}\right) x \qquad (10)$$

The slope of $d^{n/2}$ versus d yields $(K_2/K_1)^{1/2}$ and the intercept is a measure of x .The fracture toughness (K_c) is given by

$$K_c = \frac{P}{\beta C^{3/2}} \qquad (11)$$

where C is the crack length measured from the centre of the indentation mark to the crack tip, P is the applied load and geometrical constant b = 7 for Vickers' indenter. The brittleness index (B) is given by

$$B = \frac{H_V}{K_c} \qquad (12)$$

The yield strength (σ_v) of the material can be found out using the relation

$$\sigma_V = \frac{H_V}{2.9}\{1-(2-n)\}\left[\frac{12.5(2-n)}{1-(2-n)}\right]^{2-n} \qquad (13)$$

The load dependent hardness parameters n, K_1, K_2, fracture toughness K_c), brittleness index (B) and yield strength (σ_v) are calculated for the LPT crystal and are given in Table 2.

Table 2. Hardness parameters for LPT single crystal.

Parameters	Values
n	1.602
K_1 (10^6kg/m)	12.35
K_2 (kg/m)	2.72
X(μm)	5
σ_v (MPa)	182.90

6. Dielectric property

The dielectric study on single crystal was carried out using the instrument, HIOCKI 3532-50 LCR HITESTER. A sample of dimension 1 x 0.5 x 0.1 cm^3 having silver coating on the opposite faces was placed between the two copper electrodes and thus a parallel plate capacitor was formed. The capacitance of the sample has been measured by varying the frequency from 100Hz to 5 MHz and dielectric constant (ε ′) Vs applied frequency is plotted (Fig.4). The dielectric constant has higher value 1420 in the lower frequency region (50 Hz) and then it decreases to 136 with the applied high frequency (5MHz). The increase in dielectric constant at low frequency is attributed to the space charge polarization [14]. The dielectric loss is also studied as a function of frequency at different temperatures (Fig. 5). These curves suggest that the dielectric loss strongly depends on the frequency of the applied field, similar to that of dielectric constant of the ionic systems [15, 16].

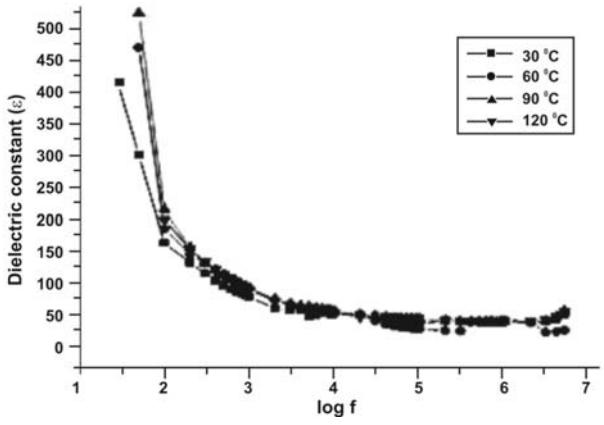

Fig. 4. dielectric constant vs log f.

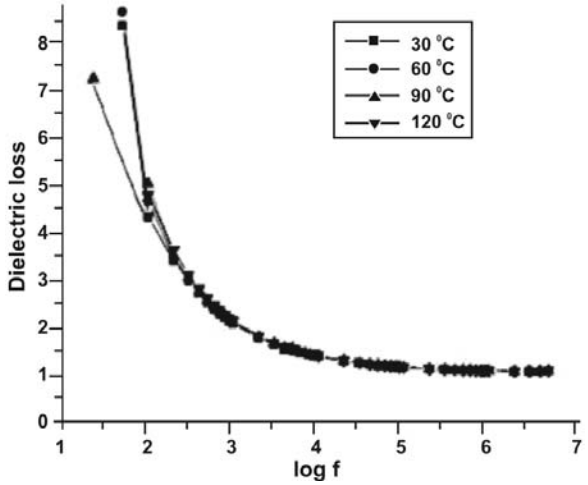

Fig. 5. dielectric loss vs log f.

7. Conclusion

Good optical quality single crystals of LPT were grown by using the slow evaporation technique. The lattice parameters were calculated by single crystal X-ray diffraction and it was confirmed that the crystals belong to the orthorhombic system with the space group P_{21}. The physical parameters such as valence electron plasma energy, Penn gap, Fermi energy and electronic polarisability have been determined for the LPT crystal. Mechanical hardness studies reveal that Vickers' hardness number increases as the load increases and then decreases for higher loads, and several hardness parameters have been calculated for the grown crystals. The variation of dielectric constant and dielectric loss were studied as a function of frequency and temperature.

References

[1] P. N. Prasad, D. J. Williams, Introduction to Nonlinear Optical Effects in Organic Molecules and Polymers, Wiley, New York, 1991.
[2] D. S. Chemla, J. Zyss, Nonlinear Optical Properties of Organic Molecules and Crystals, Academic Press, New York, 1987.
[3] T. Mallik, T. Kar, G. Bocelli, A. Musatti, Cryst. Res. Technol. **41,** 280 (2006).
[4] J. J. Rodrigues Jr., L. Misoguti, F. D. Nunes, C. R. Mendonca,S.C. Zilio, Opt. Mater. **22,** 235 (2003).
[5] E. Ramachandran, S. Natarajan, Cryst. Res. Technol. **39,** 308 (2004).
[6] M. Narayan Bhat, S. M. Dharmaprakash, J. Crystal Growth **236,** 376 (2002).
[7] T. Pal, T. Kar, Mater. Chem. Phys. **91,** 343 (2005).
[8] S. Myung, M. Pink, M.-H. Baik, David E. Clemmer, Acta Crystallogr.C**61**, 506 (2005).
[9] S. Boomadevi, R. Dhanasekaran, J. Crystal Growth. **261**, 70 (2004).
[10] S. A. Martin Britto Dhas, M. Suresh, P. Raji, K. Ramachandran, S. Natarajan, Cryst. Res. Technol. **42**, 190 (2007)
[11] S. A. Martin Britto Dhas, S. Natarajan, Cryst. Res. Technol. **42,k** 471 (2007).
[12] N. M. Ravindra, R. P.Bharadwaj, K. Sunil Kumar, V.K. Srivastava, Infrared Phys. **21**, 369 (1981).
[13] N. M. Ravindra, V. K. Srivastava, Infrared Phys. **21**, 369 (1981)
[14] J. C. Anderson, Dielectrics, Chapman and Hall, (1964).
[15] K. V. Rao, A. Smakula, J. Appl. Phys. **36**, 2031 (1965)
[16] K. V. Rao, A. Smakula, J. Appl. Phys. **37**, 319 (1966).

*Corresponding author: sureshsagadevan@yahoo.co.in