academicJournals

Vol. 8(42), pp. 1988-1993, 16 November, 2013
DOI: 10.5897/IJPS2013.4011
ISSN 1992 - 1950 © 2013 Academic Journals
http://www.academicjournals.org/IJPS

International Journal of Physical Sciences

Full Length Research Paper

Synthesis, growth and characterization of picolinic acid hydrochloride: A novel semiorganic nonlinear optical single crystal

P. Koteeswari[1], Suresh Sagadevan[2]* and P. Mani[1]

[1]Department of Physics, Hindustan University, Padur, India.
[2]Department of Physics, Sree Sastha Institute of Engineering and Technology, Chembarambakkam, Chennai, 600123, India.

Accepted 5 November, 2013

Nonlinear optical single crystals of picolinic acid hydrochloride (PHCL) were grown by the slow evaporation method. The grown crystal was subjected to a single crystal X-ray diffraction analysis, to confirm that it belongs to the orthorhombic structure. The Nonlinear Optical (NLO) property of the crystal is confirmed with the emission of green radiation from the crystal under the illumination of laser radiation (106.4 nm) from a Q switched Neodymium: Yttrium Aluminum Garnet (Nd: YAG) laser. The optical transmission range of the grown crystal was measured by Ultraviolet-Visible-Near Infrared (UV-VIS-NIR) with the lower cut-off wavelength as 195 nm. The mechanical strength of the grown crystal was analyzed using Vickers microhardness tester. The dielectric constant and dielectric loss of picolinic acid hydrochloride are measured in the frequency range of 50 Hz to 5 MHz at different temperatures.

Key words Crystal growth, Nonlinear Optical (NLO), optical transmission, single crystal X-ray diffraction (XRD), mechanical properties, dielectric studies

INTRODUCTION

The engineering of new nonlinear optical materials, structures, and devices with enhanced figures of merit has developed over the last two decades, as a major force to help drive nonlinear optics from the laboratory to real applications. The NLO process requires materials that are malleable enough to accommodate the amplitude, phase, polarizations and frequency of the optical beam. Nonlinear optics deal with the interactions of the applied electromagnetic fields in various materials to generate a new electromagnetic field, altered in phase, frequency, amplitude or other physical properties (Chemla and Zyss, 1987; Bosshard et al., 1995). The growth of high-quality single crystals remains a challenge in material science. Large sized structurally perfect crystals are required for fundamental research and practical implementation in photonic and optoelectronic technology. Semi-organic nonlinear optical single crystals have been proposed for a new approach. They have the combined properties of both inorganic and organic crystals, like high damage threshold, wide transparency range, less deliquescence and high non-linear coefficients, which make them suitable for device fabrication (Jiang and Fang, 1999). Crystals are the pillars of modern technology. The modern technology is very much dependent upon crystals such as semiconductors, piezoelectric transducers, radiation detectors, ultrasonic amplifiers, solid state lasers, acousto-optic and nonlinear optical devices. Crystal growth is a fundamental part of materials science and engineering. Since crystals of suitable size and perfection

*Corresponding author. E-mail: sureshsagadevan@yahoo.co.in

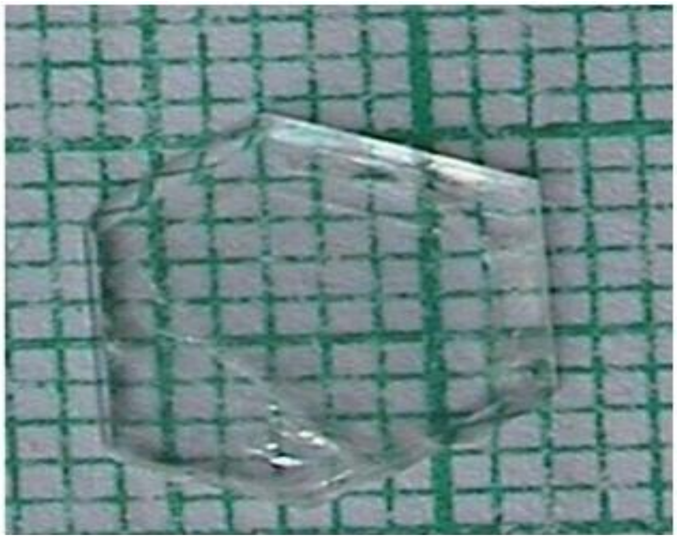

Figure 1. Photograph of grown PHCL single crystal.

are required for practical devices. Hence, this work is focused on growth and characterization of picolinic acid hydrochloride single crystals.

The grown crystal was characterized using the single crystal X-ray diffraction (XRD), UV-VIS-NIR spectral analysis, microhardness and dielectric studies. The lattice parameters and crystal structure of the grown crystal was confirmed using single crystal X-ray diffraction analysis. The NLO property of the crystal is confirmed with the emission of green radiation from the crystal under the illumination of laser radiation (106.4 nm) from a Q switched Nd: YAG laser. The optical transmission study reveals the transparency of the crystal in the entire visible region and the cut off wavelength has been found to be 195 nm. Vicker's microhardness test enumerating the mechanical strength of the crystal has been determined. The dielectric constant and dielectric loss measurements were carried out at different temperatures and frequencies.

EXPERIMENTAL PROCEDURE

In general the nonlinear materials are used in the fields of optoelectronics and photonics. For this we require the materials in single crystalline form. For growing single crystals of amino acid materials slow evaporation method is employed in the present work. The growth of good quality single crystals by slow evaporation technique require optimized conditions and same may be achieved with the help of the following ways:

(i) Material purification
(ii) Solvent selection and solubility
(iii) Crystal habit
(iv) Crystallization apparatus
(v) Preparation of saturated solution

Picolinic acid hydrochloride single crystals were synthesized by dissolving picolinic acid and hydrochloric acid in the molar ratio of 1:1 in distilled water. The solution was stirred continuously using a magnetic stirrer. The prepared solution was filtered and kept undisturbed at room temperature. Tiny seed crystals with good transparency were obtained due to spontaneous nucleation. Among them, a defect free seed crystal was suspended in the mother solution, which was allowed to evaporate at room temperature. Large sized single crystals have been obtained due to the collection of monomers at the seed crystal sites from the mother solution. Figure 1 shows the photograph of as-grown picolinic acid hydrochloride single crystal.

RESULTS AND DISCUSSION

Single crystal XRD

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. The calculated lattice parameters are; a = 13.79Å,b = 6.54Å, c = 7.76 Å and the volume of the crystal V = 1232 $Å^3$. The crystal belongs to the orthorhombic system with space group $P2_12_12_1$.

Optical transmission studies

Figure 2 shows the optical transmission spectrum of the picolinic acid hydrochloride single crystal, recorded in the wavelength region ranging from 200 to 1000 nm. The UV cut off wavelength for the grown crystal was found to be 195 nm.

Vickers microhardness test

An analysis of the mechanical property of the grown

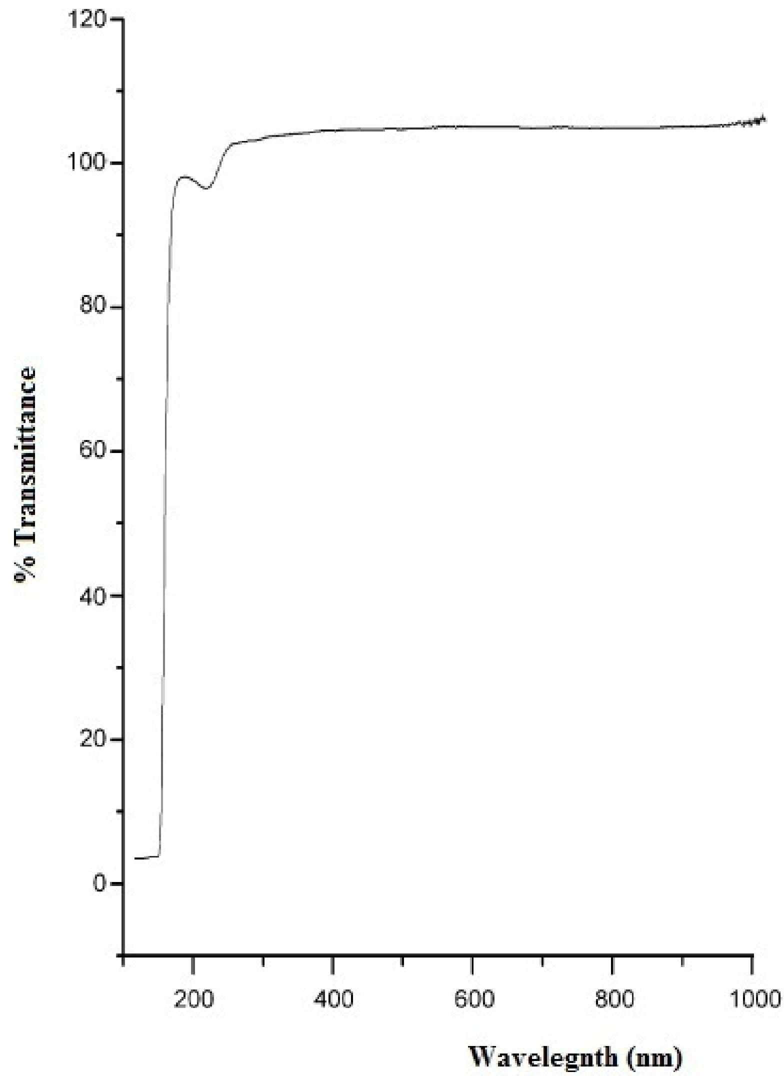

Figure 2. UV-VIS-NIR transmission spectrum.

crystal is also important for the fabrication of electronic and optical devices. Microhardness studies were carried out on a selected very transparent single crystal using the microharness tester, fitted with a Vickers diamond pyramidal indenter (Mott, 1958). To get the exact results of the hardness of the grown crystal, indentations were made on the picolinic acid hydrochloride crystals with applied load ranging from 10 to 50 g. The time of indentation has been kept constant for 10s. Five indentations were made on each surface under test for the same load and the mean diagonal length was measured. To deflect the surface defects, the distance between consecutive indentations was kept as more than five times the diagonal length of the indentation mark. The diagonal length of indentation mark has been assessed using a micrometer eyepiece. The values of Vicker's microhardness at different loads were calculated using the relation:

$$Hv = 1.8544\, P / d^2 kg / mm^2 \quad (1)$$

where, P is the applied load and d is the mean diagonal length of the indenter impression. Figure 3 shows the variation of hardness with the applied load. It is observed that the hardness of picolinic acid hydrochloride increases by increasing the load up to 50 g, which indicates the reverse indentation size effect (Zhao et al., 2006; Karan and Gupta, 2005). The increasing trend of microhardness with the load up to 50 g is well understood from the Mayer's law and Onitisch condition. According to Mayer law, the relationship between the load (P) and the size (d) of the indentation is given as

$$P = kd^n \quad (2)$$

where, n is called the Mayer index or work hardening

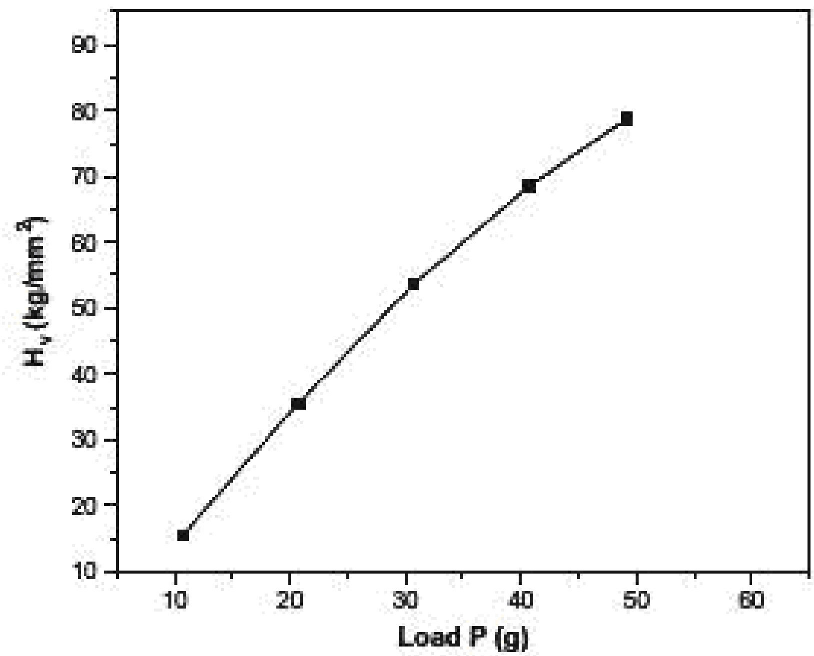

Figure 3. Vickers microhardness of PHCL Crystal.

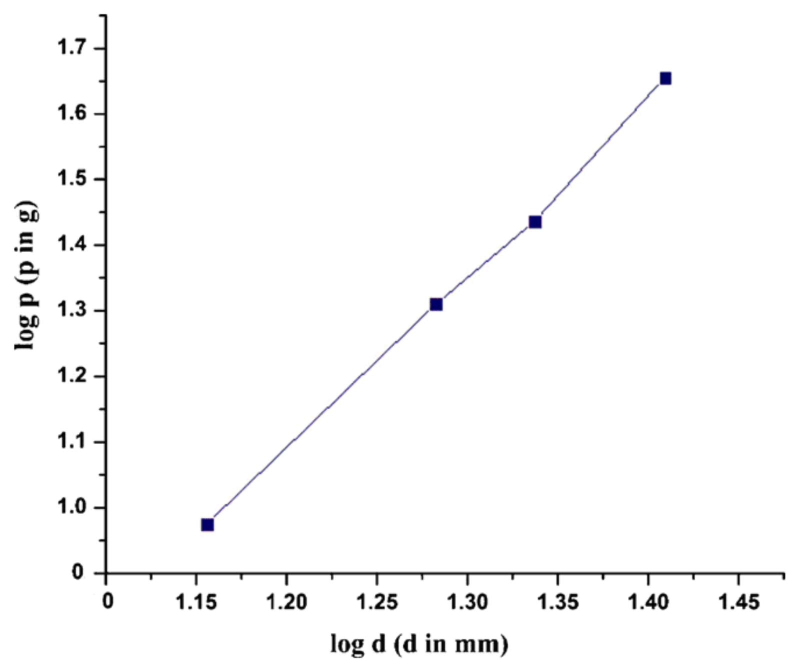

Figure 4. Plot of log d vs log P.

index. Hence, the slope of the plot of log d versus log P will give the work hardening index. The slope of the plot for PHCL (Figure 4) is found to be 2.6. According to Onitisch if n is greater than 2, the microhardness will increase with the increase in the load. Hence, the material shows an increasing trend for the hardness of the material up to a particular load 50 g. Since, picolinic acid hydrochloride has a moderately higher value of the hardness number, the material is found to be suitable for device fabrications. Thus, picolinic acid hydrochloride

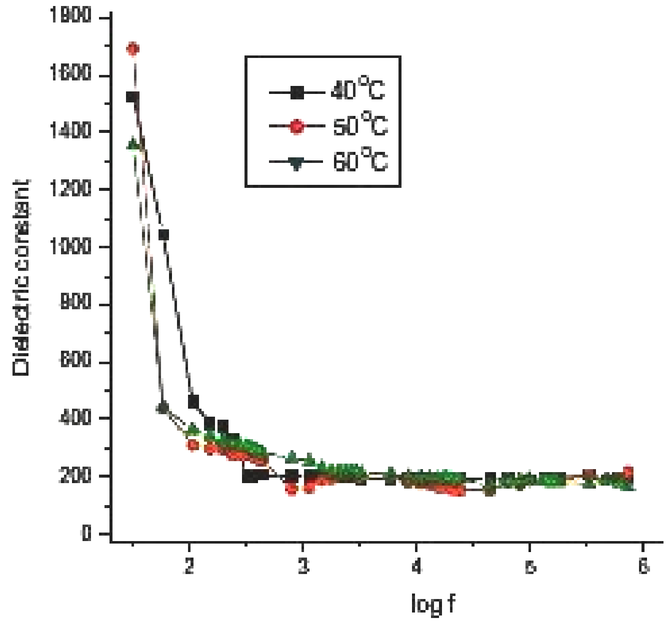

Figure 5. Variation of dielectric constant with log frequency.

crystals belong to the soft-material category. It shows that the grown crystal can be used for devices, which can withstand thermal local stresses.

Dielectric properties

Dielectric studies are an important characteristic that can be used to bring knowledge based on the electrical properties of a material medium as a function of temperature and frequency. Based on this analysis, the capability of storing electric charges by the material and that of transferring the electric charge can be measured. Dielectric properties are correlated with the electro optic property of the crystals: particularly when they are non-conducting materials. The microelectronics industry needs low dielectric constant (*εr*) materials as an interlayer dielectric (Hatton et al., 2006). The study of the dielectric constant of a material gives an outline about the nature of atoms, ions and their bonding in the material. From the analysis of the dielectric constant and dielectric loss as a function of frequency and temperature, the different polarization mechanism in solids can be understood. The dielectric constant and the dielectric loss of the picolinic acid hydrochloride crystal were studied at different temperatures using the HIOKI 3532 LCR HITESTER in the frequency region of 50 Hz to 5 MHz. The dielectric constant was measured as a function of frequency at different temperatures ranging from 40, 50, to 60°C and is shown in Figure 5, while the corresponding dielectric losses are depicted in Figure 6. The dielectric constant is evaluated using the relation,

$$\varepsilon_r = \frac{Cd}{\varepsilon_0 A} \tag{3}$$

where *d* is the thickness of the sample, *A*, the area of the sample. Figure 5 shows the plot of the dielectric constant (ε) versus log frequency for 40, 50 to 60°C. It is seen that the value of the dielectric constant is high in the lower frequency region for all the temperatures and then it decreases with an increase in the frequency. The high value of the dielectric constant at low frequency region is attributed to space charge polarization due to charged lattice defects (Smyth, 1965). A graph is drawn between the dielectric loss and log frequency for different temperatures (40, 50, and 60°C) and is shown in Figure 6. The low value of the dielectric loss at a high frequency suggests that the grown crystals possess good optical quality. This parameter is of vital importance for nonlinear optical materials in their applications (Balarew and Duhlew, 1984). The variation at low temperature is mainly due to the crystal expansion and electronic and ionic polarizations. The variation at high temperatures is mainly attributed to thermally generated charge carriers and impurity dipoles. This behaviour is useful for the fabrication of microelectronic and nonlinear optical devices.

Second Harmonic Generation (SHG) efficiency test

The SHG conversion efficiency of PHCL was determined by Kurtz's Perry technique. The crystal was ground into

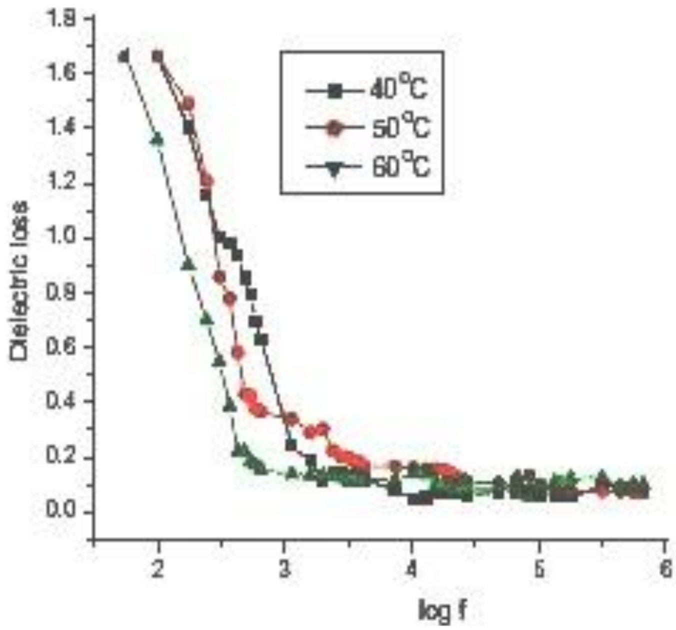

Figure 6. Variation of dielectric loss with log frequency.

very fine powder and tightly parallel in a microcapillary tube. Then it was mounted in the path of Nd: YAG laser beam of energy 1.95 mJ/pulse. When KDP crystal was used as a reference material, it produced 65 mV as output beam of voltage. But it was about 102 mV for the grown sample and hence it is confirmed that the material has NLO efficiency of about 1.6 times that of KDP crystals.

Conclusion

A picolinic acid hydrochloride single crystal was successfully grown by the slow evaporation technique at room temperature. The single crystal XRD study reveals that the picolinic acid hydrochloride crystal has an orthorhombic structure with space group $P2_12_12_1$. The Kurtz powder test confirms that the SHG efficiency of PHCL is higher than that of KDP. The optical transmission spectral analysis reveals that the crystal is transparent in the entire UV-VIS-NIR region with the lower cut-off wavelength as 195 nm. Its mechanical behaviour has been studied by the Vicker's microharness test. The dielectric measurements indicate that the dielectric constant and dielectric loss of the picolinic acid hydrochloride single crystal decreases with increasing frequency significantly to make the crystal a more interesting material in the microelectronics industry.

REFERENCES

Balarew C, Duhlew R (1984). Application of the hard and soft acids and bases concept to explain ligand coordination in double salt structures, J. Solid State Chem. 55:1-6.
Bosshard CH, Sutter K, Pretre PH, Hulliger J, Florsheimer M, Kaatz P, Gunter P (1995). Organic nonlinear optical materials, Advances in Nonlinear Optics, Gordon and Breach, Amsterdam.
Chemla S, Zyss J (1987). Nonlinear Optical Properties of Organic Molecules and Crystals, Academic Press, New York.
Hatton BT, Landskron K, Hunks WJ (2006). Materials Chemistry for Low-K Materials, Mater. Today, 9:22-31.
Jiang MH, Fang Q (1999). Organic and Semiorganic Nonlinear Optical Materials. Adv. Mater. Weinheim, Germany. 13:1147-1151.
Karan S, Gupta PS (2005). Vickers microhardness studies on solution grown single crystals of magnesium sulphate hepta-hydrate, Mater. Sci. Eng. A. 398:198–203.
Mott BW (1958). Hardness of Butter, Influence of Season and Manufacturing Method Micro indentation hardness testing, J. Dairy Sci. 41:360-368.
Smyth CP (1965). Dielectric Behavior and Structure, McGraw-Hill, New York, 1965.
Zhao L, Li SB, Wen GA, Peng B, Huang W (2006). Imidazole derivatives: Thermally stable organic luminescence materials, Mater. Chem. Physics. 100:460-463.