Research Article

Studies on the synthesis, growth and physic - chemical properties of a new single NLO crystal: potassium L-threoninate

S Anna Venus[a], S Anbarasu[a], Prem Anand Devarajan[b*]

[a]Physics Research Centre, [b]Assistant Professor, Department of Physics, St. Xavier's College (Autonomous), Palayamkottai-627002, Tirunelveli-627002, Tamil Nadu, INDIA.
Email: dpremanand@yahoo.co.in

Abstract

Potassium L - threoninate (PLT), a New Second order non linear optical crystal was grown by slow evaporation method for the first time. The unit cell parameters of as the grown crystal was estimated by single crystal X-ray diffraction technique. The as grown crystal was subjected to X-ray Powder diffraction studies to identify the crystalline nature. The UV-Vis absorption spectra was recorded to estimate the cut-off wavelength. The presence of functional groups were ascertained by FTIR analysis. The thermal stability of the crystal was determined by TG/DT analysis. The hardness of the crystal was studied by Vickers micro hardness tester. The SHG efficiency was tested by Kurtz Powder method. Dielectric measurements were carried out at various temperatures in the frequency range 20 Hz to 1 MHz. The AC conductivity measurements done on PLT reveals that PLT crystal has a sharp electrical conductivity with an increase of temperature.
Keywords: AC conductivity, Dielectric properties, Fourier transform infrared (FTIR), Micro Hardness, NLO, Potassium L - threoninate (PLT), TG/DTA, UV-vis-NIR and X-ray diffraction.

[*]**Address for Correspondence:**
Dr. Prem Anand Devarajan, Physics Research Centre, Department of Physics, St. Xavier's College (Autonomous), Palayamkottai-627002, Tirunelveli-627002, Tamil Nadu, INDIA.
Email: dpremanand@yahoo.co.in
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INTRODUCTION

Nonlinear optical materials are expected to play a major role in photonics pertaining to optical information processing, telecommunication sensor protector applications, optical data storage, etc. Some organic compounds exhibit large NLO response, in many cases, order of magnitude larger than widely known inorganic materials. They also offer the flexibility of molecular design and the promise of virtually an unlimited number of crystalline structures. In this stimulating context, organic nonlinear materials have been recognized as a forefront candidate for fundamental and applied investigations involving, in a joint effort, chemists, material scientists and optical engineers[1-5]. This research is extended to semi-organic NLO material crystal so as to obtain superior NLO crystal by combining the advantages of organic and inorganic materials. Hence Semi-organic single crystals are attracting great attention in the field of non linear optics because of their high optical nonlinearity, chemical flexibility of ions, high mechanical strength, thermal stability and excellent transmittance in the UV-Vis region[6-8]. Moreover amino acid family crystals are still gaining importance because of its high second order nonlinear optical coefficients, wide optical transparency and multifunctional substitutions[9-10]. Most of the amino acids individually exhibit the NLO property due to donor amino group NH_3^+ and acceptor carboxyl group COO^- and intermolecular charge transfer[11]. Therefore, amino acid enhances the material properties such as nonlinear and ferroelectric properties[2]. L-threonine is an important polar amino acid, which shows higher SHG than other amino acids[12]. Several compounds of L-threonine have been reported[13-14]. Over the past two decades, there has been remarkable interest in growth and

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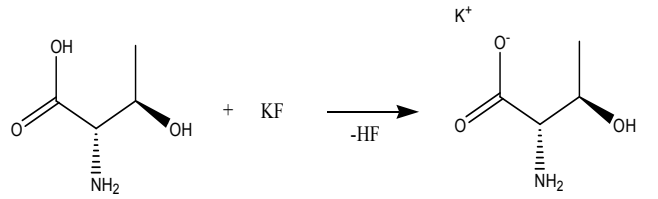
characterization of pure L-threonine[15-17] and related compounds of L-threonine[18-20]. In the present work, investigations are carried out to study the physico–chemical properties on the growth, optical, thermal, dielectric and mechanical properties of PLT and it is found to have promising properties for potential SONLO applications. The as grown PLT single crystals were subjected to XRD, PXRD, UV-vis-NIR, FTIR, TG/DTA, Dielectric, AC conductivity and micro hardness studies for the first time.

MATERIALS AND METHODS

Synthesis

The appropriate stoichiometric amount of L-threonine and Potassium fluoride was taken with excess of doubly deionized water to synthesize PLT. The reaction scheme is shown in Figure1. The as said reagents were dissolved in deionized water and saturated PLT solution was prepared at room temperature. This saturated solution was placed in a constant temperature bath kept at the desired growth temperature.



L-Threonine Potassium L-Threoninate

Figure 1: Reaction scheme for Potassium L-threoninate

Solubility

The solubility of pure PLT in water has been determined for five different temperatures 30, 35, 40, 45 and 50˚C respectively. Recrystallized salt was used for these studies. The solubility was determined by dissolving the solute in water, ethanol and methanol in an air tight container maintained at a constant temperature with continuous stirring. It was found that deionized water as the best solvent. After attaining the saturation, the equilibrium concentration of the solution was analyzed gravimetrically. The solubility curve for PLT is shown in Figure 2. It is seen from the solubility curve that PLT increases with increase in temperature.

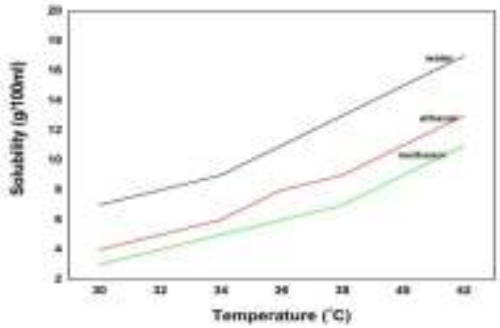


Figure 2: Solubility curve of PLT single crystal

Crystal growth

Single crystals of PLT was grown by preparing saturated solution in deionized water at room temperature and stirred well to yield a homogeneous mixture of solution. The solution was then filtered twice to remove the suspended impurities and allowed to evaporate slowly in a constant temperature bath kept at 36℃, which resulted gradually in supersaturation. Crystals of well optical transparency with the dimension 10 mm x 3 mm x 2 mm have been harvested. The photograph of as grown single crystal of PLT is shown in Figure 3.

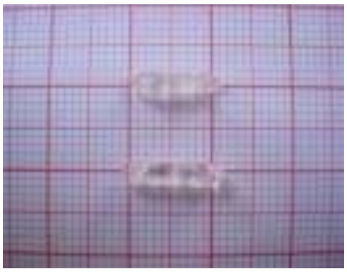


Figure 3: Photograph of as grown crystals of Potassium L-threoninate (PLT) single crystal

Instrumentation

A grown PLT single crystal was subjected to single crystal X-ray diffraction studies using ENRAF NONIUS CAD-4 X-ray diffractometer with MoKα (λ=0.71069 Å) radiation to evaluate the lattice parameter values. Powder X-ray Diffraction (PXRD) pattern of the powdered sample of PLT was obtained using a powder X-ray diffractometer (PANalytical Model, Nickel filtered Cu Kα radiations with λ= 1.54056 Å at 35 kV, 10 mA) to ascertain the crystallinity and purity of the as-grown crystal. UV-visible transmission spectrum of PLT was obtained using Shimadzu UV-1800 UV-vis-NIR spectrometer in the range from 190 nm to 900 nm. The Fourier transform infrared spectrum was recorded in the region 400-4000 cm-1 with Perkin Elmer Fourier transform infrared spectrometer (Model : Spectrum RX9) using KBr pellet containing PLT powder obtained from the grown single crystal. Atomic Absorption

Spectroscopy and CHN analysis were carried out to confirm the elements present in the synthesized PLT crystal. Thermogravimetric and differential thermogravimetric analysis was performed using Seiko thermal analyzer in the terperature range 30-600˚C in nitrogen atmosphere at a heating rate of 10˚C/min to investigate the thermal behaviour of the grown crystals. The dielectric and AC conductivity studies were done using HIOKI 3532 LCR Hitester in the frequency range of 100 Hz – 1 MHz. Mechanical property was studied by measuring microhardness of the grown PLT crystal and this was carried out using Vickers microhardness tester fitted with a diamond indenter. Smooth, flat surface was selected and subjected to this study. Indentations were made for various loads from 1 g to 100 g. To confirm the nonlinear optical property, Kurtz and Perry powder SHG test was carried out for the grown crystal using Nd:YAG Q-switched laser which emits the first harmonic output of 1064 nm.

RESULTS AND DISCUSSION

Single crystal X-ray diffraction

The crystals were subjected to X-ray diffraction in an ENRAF Nonius CAD 4 diffractometer with MoKα radiation of λ= 0.71073Å. The unit cell parameters obtained are a = 5.8 Å, b = 8.3 Å, c = 13.19 Å, α = β = γ =90˚, Volume = 634.96 $Å^3$ with the orthorhombic system of $P2_12_12_1$ space group.

Powder X-ray diffraction

The Powder X-ray diffraction studies were carried out using powder X-ray diffractometer (P Analytical XPERT PROMPO) with CuKα (λ=1.5406Å) radiation. Powder XRD pattern was recorded by scanning the sample over the range 6˚ - 60˚ at the rate of 2˚ per minute. The recorded XRD pattern with hkl indices of PLT crystals is shown in Figure 4. The appearance of sharp and strong peaks confirms the good quality of the grown crystals.

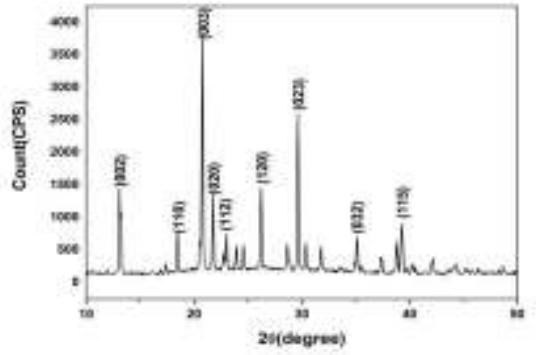


Figure 4: PXRD spectrum of PLT single crystal

UV-vis-NIR spectral analysis

Optical absorption analysis was studied out at room temperature by Shimadzu UV-1800 UV-vis-NIR spectrometer. The optical absorption spectrum of PLT was recorded in the range 190 – 900 nm. Figure 5 shows that the crystal has a wide transmission of about 100% in the entire range without any absorption peak. The lower cut off wavelength of PLT was found to be 220 nm. The crystal has good optical transmission in the visible region. The transparency in the visible region for the crystal suggests its suitability for second harmonic generation. The measured transmittance (T) was used to calculate the absorption coefficient (α) using the relation

$\alpha = \{2.3026\log(1/T)\}/t$

where t is the thickness of the sample. The optical band gap (E_g) is related to optical absorption coefficient (α) and energy (hν) of the incident photon given by

$\alpha = \{A(h\nu - E_g)^{1/2}\}/ h\nu$

where A is a constant, Eg is the optical band gap, h is the Planck's constant and ν is the frequency of the incident photons. The band gap of PLT crystal was estimated by plotting $(\alpha h\nu)^2$ versus hν as shown in Figure 6. From the Figure, the value of band gap was found to be 5.5 eV.

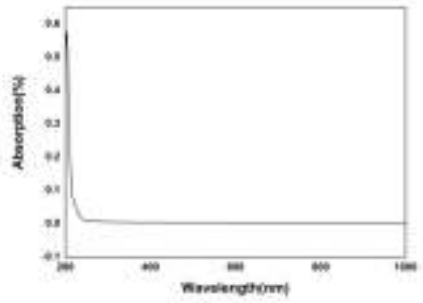


Figure 5: Optical absorption spectrum

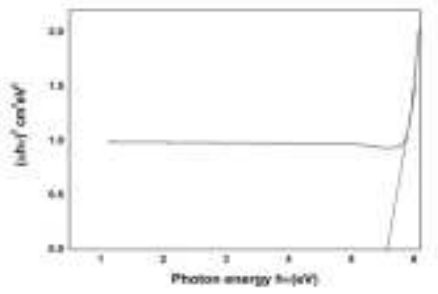


Figure 6: Tauc's plot

FTIR spectroscopic analysis

The FTIR spectra of the sample was recorded in the frequency region of 400 – 4000 cm^{-1} using PERKIN ELMER RX9 FTIR Spectrometer to confirm the vibrational structure of the grown crystalline compound. Figure 7 shows the FTIR spectrum of PLT. The sharp

band at 869.84 cm^{-1} is related to a stretching of CCN structure. Due to the stretching vibration involving carbon and nitrogen of the amino group there exists a peak at 1041.49 cm^{-1}. The rocking of NH_3^+ structure is observed at wave numbers 112.85 and 1184.21 cm^{-1}. Bending vibrations of CH group are found in PLT with peaks at 1247.86, 1317.29 and 1346.22 cm^{-1} in the spectrum. The stretching vibrations also exist in both the NH_3^+ and CH structures. The NH_3^+ stretching vibrations are present in all amino acids. Here the stretching vibration of NH_3^+ may be assigned to the vibration at 2975.96 cm^{-1}. The asymmetric stretching of the NH_3^+ is observed with wave number 3166.9 cm^{-1}. The other vibrational assignments of PLT single crystals are given in Table 1.

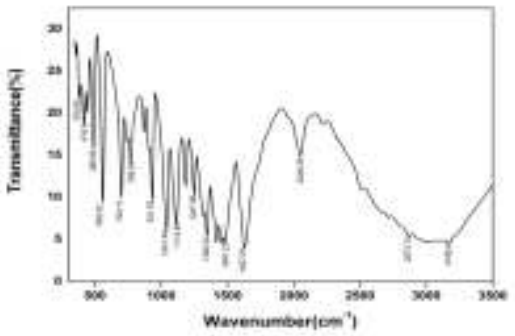


Figure 7: FT-IR spectrum of PLT single crystal

Table 1: Vibrational assignments of PLT crystal

Sr. No	Wavenumber (cm^{-1})	Assignments
1	489.89	Torsional oscillation of NH_3^+
2	559.32	Rocking COO^-
3	700.11	Wagging vibration of COO^-
4	744.47	Torsion of COH
5	769.54	COO^- bending
6	931.55	C-C stretching
7	1415.65	Symmetric stretching of COO^-
8	1456.16	CH_3 bending
9	1481.23	NH_3^+ bending
10	1627.81	Asymmetric bending of NH_3^+

Elemental analysis

To confirm the chemical composition of the synthesized compound, we carried out AAS (Atomic Absorption Spectroscopy) and CHN analysis on the recrystallised sample using the instrument Elementer vario ElIII microanalyzer to ascertain the presence of potassium in the as grown crystals of PLT. The presence of Fluorine is not identified due to the absence of fluorine in the crystal lattice. The results of the analysis are presented in Table 2. Theoretical values of C, H, N and K were found by the molecular formula $K^+C_4H_8NO_3$. The experimental and calculated values of C, H and N agree with each other confirming the formation of PLT.

Table 2: Elemental analysis of PLT

Element	Experimental	Calculated
Carbon	31.92	30.57
Hydrogen	5.12	5.09
Nitrogen	9.87	8.91
Potassium	23.29	24.84

TG/DT analysis

Simultaneous thermogravimetry (TG) and differential thermogravimetry analysis (DTA) of powdered sample were performed in the temperature range of 30 – 600˚C, using Seiko Thermal Analyzer a with a heating rate of 10℃/min. Figure 8. Shows the TG/DTA curve, only one major loss of weight exists in the TG curve, which might be due to the decomposition of the PLT single crystal. The decomposition starts at 221.9℃. There is no phase transition process before 221.9˚C, namely, the crystal is stable up to 221.9˚C which is a higher temperature than for many other semi organic NLO crystals.

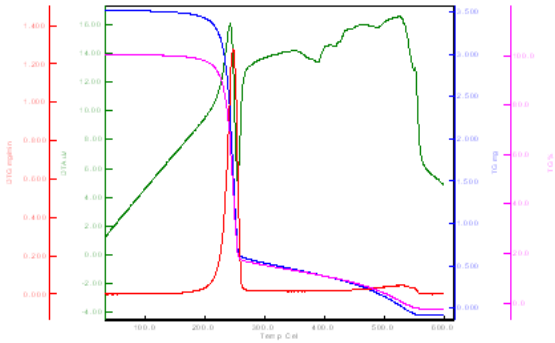


Figure 8: TG/DT curve of PLT single crystal

Dielectric studies

The dielectric constant and dielectric loss measurements were made using HIOKI 3532 LCR Hitester in the frequency range of 100 Hz – 1MHz. Silver coatings were applied on the opposite sides of the polished crystals and placed between two copper electrodes to form a parallel plate capacitor. The dielectric constant was calculated using the relation

$$\varepsilon_r = [A_{air}/A_{cry}] \{C_{cry} - C_{ir}(1 - A_{cry} / A_{air})/ C_{air}\}$$

Where A is the area of the sample and C is the capacitance of the crystal. The observations were made while cooling the sample in the frequency range 20Hz to 1MHz at the temperature of 50 to 150℃. Figure 9 and Figure 10 shows the plot of dielectric constant (ε_r) as a function of frequency and dielectric loss (D) as a function of log frequency respectively. It is observed that the ε_r and D are both inversely proportional to frequency. This is a normal dielectric behavior[21] that both ε_r and D decrease with increasing frequency. This can be understood on the basis of the mechanism of polarization which is similar to that of conduction process. The

electronic exchange of the number of ions in the crystal gives local displacement of electrons in the direction of the applied field which in turn gives rise to polarization[22]. It is seen from the Fig.9, that the dielectric constant has higher values in the lower frequency region and then it decreases with the applied frequency. The very high value of ε_r and low frequencies may be due to the presence of all the four polarization namely space charge, orientational, electronic and ionic polarization and its low value of at higher frequencies may be due to the loss of significance of these polarization gradually[23]. Dielectric loss is also studied as a function of frequency at various temperatures and is shown in Figure 10. These curves suggest that the dielectric loss strongly depends on the frequency of the applied field, similar to that of dielectric constant. This behavior is common in the case of ionic system[24-25]. The low value of dielectric loss indicates that the grown crystals are of moderately good quality.

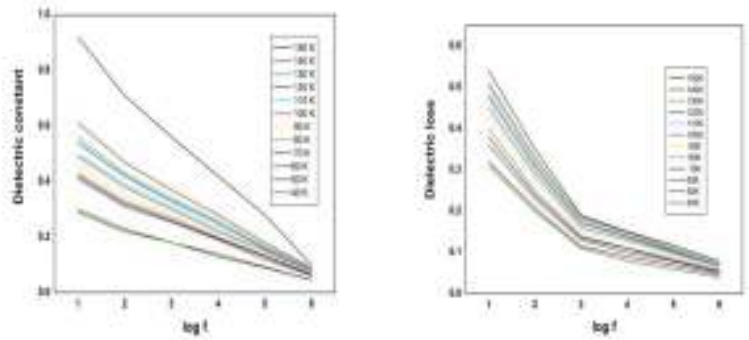


Figure 9: Variation of dielectric constant **Figure 10:** Variation of dielectric loss

AC conductivity studies

The AC conductivity studies of PLT single crystal was performed using an instrument LCR meter in a temperature range from 50-150℃. The AC conductivity graph is shown in Figure 11. It is seen from the graph that the conductivity increases when the temperature increases. Therefore defects concentration increases when the temperature rises. At higher frequencies, the increased conductivity could be due to the reduction in the space charge polarization. As seen from the dielectric graph, it may be said that the dielectric constant of the dispersive medium decreases because the term contributing to dielectric constant from ion-dipole- interaction is compensated by the thermal energy leading to the relaxation of polarization[26]. Hence the increase in conductivity of higher frequencies for a given temperature confirms small polaron hopping in the crystal[27]. The AC conductivity of PLT single crystal increases on increasing the frequency. The electrical conduction in dielectrics is mainly a defect controlled process in the low temperature region.

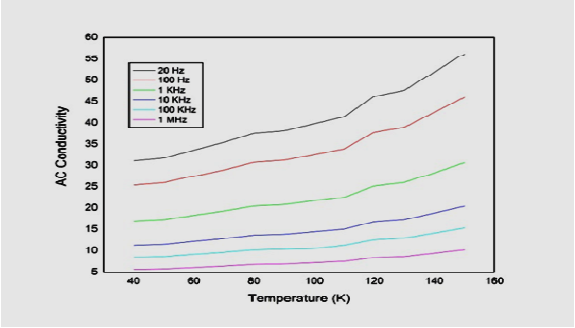


Figure 11: Variation of ac conductivity versus temperature of PLT single crystal

Microhardness Studies

Microhardness measurements were done using a Vickers's microhardness indenter using Leitz Weitzier Hardness Tester. The indentation time was fixed as 10 s. The mechanical properties of the grown crystal was studied by Vickers hardness test. The applied loads are 1, 3, 5. 10, 25, 50 and 100 g and hardness was calculated using the relation

$$H_v = 1.8554 \frac{P}{d^2} \text{ Kg mm}^{-2}$$

Where P is the load applied in kg and d is the diagonal length of the indented impressions in mm. A plot between the load P and hardness number H_V is shown in Figure 12, which shows that the microhardness number increases with increasing load for the grown crystal. The graph between log p against log d for PLT crystals are shown in

Figure 13. The slope of the straight line gives the work hardening coefficient (n). The value for the work hardening coefficient for PLT crystal is 2.979. According to Onitsch[28], if n is greater than 1.6, the crystal belongs to soft category. As n is greater than 1.6, PLT crystal is a soft material and the hardness number increases with the load is also observed.

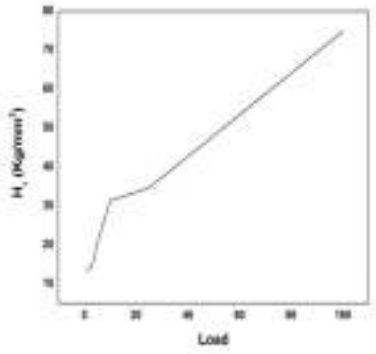


Figure 12: Variation of Hv with load

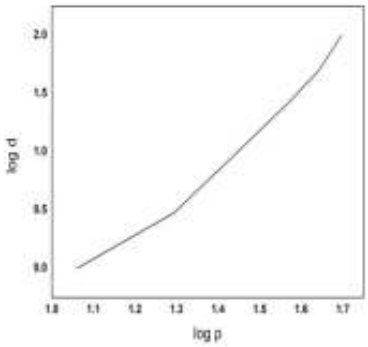


Figure 13: Plot between logP and log d

NLO Test

The SHG behaviour of the powdered material was tested using Kurtz and Perry method[29]. The sample was ground into very fine powder and tightly packed in a micro capillary tube. Then it was mounted in the path of Nd:YAG laser beam of 9.6 mJ/pulse energy obtained by splitting the original laser beam. The output light was passed through a monochromator which detected green light at 532 nm. This confirms the NLO behavior of the material. The green light intensity was registered by a photomultiplier tube and converted into an electrical signal. This signal was displayed on the oscilloscope screen. The sample was replaced by potassium dihydrogen ortho phosphate (KDP) and the signal was displayed in the oscilloscope screen. SHG conversion efficiency was computed by the ratio of signal amplitude of the PLT crystal to that of the KDP signal amplitude recorded for the same input power. The SHG relative efficiency of PLT crystal was found to be 1.7 times higher than that of KDP.

CONCLUSION

A new nonlinear semi organic SONLO crystal PLT was successfully grown employing slow solvent evaporation technique. A convenient size of 10 mm x 3 mm x 2 mm was harvested in a month time. The solubility of PLT single crystal was estimated to be 10 g in 100ml of water at room temperature. The UV-VIS- NIR spectral analysis showed good transparency in the UV and visible region. The various functional groups in PLT crystal was identified using FTIR analysis. From TG/DT analysis thermal stability of the grown crystal was observered up to 221.9˚ C. The dielectric constant and dielectric loss measurements of PLT crystal revealed the normal behavior. AC conductivity studies performed on PLT single crystal establishes the mechanism of polarization. Micro hardness study reveals that the grown PLT single crystal belongs to soft material and its hardness number increases with increase of loads. The SHG relative efficiency of PLT single crystal was found to be 1.8 times higher than that of KDP.

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