Growth and characterization of NLO crystal: L-leucine phthalic acid potassium iodide

JAGADEESH M.R.¹, SURESH KUMAR H.M.²*, ANANDA KUMARI R.³

¹ Department of Physics, G M Institute of Technology, Davangere-577 006, India

² Department of Physics, Siddaganga Institute of Technology, Tumkur-572 103, India

³Department of Physics, Sri Siddaganga College for Women, Tumkur-572 103, India

A new semi-organic non linear optical crystal, L-leucine phthalic acid potassium iodide (LLPPI) has been grown from an aqueous solution by slow evaporation method. The grown crystals were subjected to different characterizations, such as single crystal XRD, FT-IR, UV-Vis, TGA, SEM, EDAX, micro hardness, dielectric and powder SHG. Single crystal structure was determined from X-ray diffraction data and it revealed that the crystal belongs to triclinic system with the space group P1. The vibrational frequencies of various functional groups were derived from FT-IR spectrum. Thermal stability of the grown crystal was investigated by TG-DTA studies and it was observed that the crystal was thermally stable up to 192 °C. Optical absorption study was carried out and a good transparency in the entire visible region was observed at the lower cutoff wavelength of 227 nm. Dielectric study was performed as a function of frequency and normal dielectric behavior was observed. The micro hardness test was carried out and the load dependent hardness was measured. Kurtz powder method was employed to explore the NLO characteristics of the grown crystal.

Keywords: semi-organic crystal; slow evaporation method; NLO crystal; thermal and SHG studies

© Wroclaw University of Technology.

1. Introduction

In recent years, continuous efforts have been in progress in the field of nonlinear optics in order to design and study new materials with large nonlinear optical susceptibility. Such materials find widespread applications, such as optical switching, high speed information processing, optoelectronic modulators and frequency converters [1-3]. These applications depend on the various properties of materials, like transparency, refractive index, dielectric constant, chemical and thermal stability.

In this context, many organic, inorganic and semi-organic NLO crystals are investigated. Much attention has been paid towards organic NLO crystals due to flexibility of their molecular design and inherent ultrafast response time. But these materials are impeded by their poor mechanical and thermal properties for device fabrications. Pure inorganic NLO materials typically have excellent mechanical and thermal properties but possess relatively modest optical nonlinearity because of lack of extended π -electron delocalization. In semi-organic materials, the combination of chemical flexibilities of organics and favorable physical properties of inorganics resulted in the improved chemical stability and mechanical strength [4].

In the family of organic materials, amino acids are considered to be interesting materials for NLO devices as they contain donor carboxylic (COOH) group and the proton acceptor amino (NH₂) group. Meanwhile, inorganic derivatives of amino acids have proven to be the building blocks, which offered a wide choice of potential materials for NLO device fabrications [5–7]. L-leucine is an essential branched chain of alpha amino acid. Growth and NLO studies of L-leucine were reported earlier and the SHG efficiency of L-leucine is twice that of urea [8]. L-leucine nitrate [9], L-leucinium oxalate [10], L-leucinium perchlorate [11] and

^{*}E-mail: sureshkumarhm@rediffmail.com

L-leucine L-leucinium picrate [12] are few derivatives of L-lecucine reported earlier. Phthalate crystals are often used as diffracting crystals since they can be easily cleaved and are potential candidates for many device applications [13–15]. The study on crystal growth of potassium iodide crystal obtained by solution growth method revealed the reduction in the impurity concentration compared to melt growth technique [16]. Hence, in this paper, it is reported on the synthesis and growth of Lleucine phthalic acid potassium iodide single crystal followed by characterizations, like XRD, FT-IR, TG-DTA, UV, EDAX, SEM. Dielectric properties hardness and NLO studies and their results are discussed in detail.



Fig. 1. The photograph of the as grown crystal of LLPPI.

2. Synthesis and crystal growth

LLPPI single crystals were synthesized by taking L-leucine, phthalic acid and potassium iodide (analar grade) in the stoichiometric ratio 1:1:1. The calculated amounts of the reactants were thoroughly dissolved in a desired amount of aqueous solution and stirred well for about four hours using a magnetic stirrer. The solution was then filtered using a whatmann filter paper and was transferred to a petri dish and the crystallization was allowed to take place by slow evaporation of the solvent at room temperature. By continuous evaporation of the solvent, a good quality seed, optically well shaped transparent crystals up to the dimension $7 \times 5 \times 3$ mm³ were obtained from the saturated mother solution over the period of 25 days. The photograph of the as grown crystal is shown in Fig. 1.

3. Results and discussions

3.1. Single crystal X-ray diffraction analysis

Bruker smart Apex Duo single crystal X-ray diffractometer was employed to collect the single crystal X-ray data of LLPPI crystal. The data revealed that the title compound crystallized in triclinic system with non centrosymmetric space group P1. The cell parameters were a = 5.13 Å, b = 7.66 Å, c = 9.70 Å, $\alpha = 89.19^{\circ}$, $\beta = 86.96^{\circ}$, $\gamma = 70.44^{\circ}$ and cell volume V = 358 Å³.



Fig. 2. Powder X-ray diffrcation pattern of LLPPI.

3.2. Powder X-ray diffraction studies

Well ground crystal samples have been analyzed using Bruker AXS D8 Advanced powder X-ray diffractometer with CuK α ($\lambda = 1.5418$ Å). Typical 2 θ scan range was made from 10° to 45° with a scan speed of 2° per minute. From this diffraction data various planes of reflections were observed and the resulting powder X-ray diffraction pattern is shown in Fig. 2. The pattern is clearly showing the good crystalline nature of the grown crystals.

3.3. FT-IR spectral analysis

The FT-IR spectrometry measurement was done with a Perkin Elmer spectrophotometer using KBr pellet technique in the range of 400 to 4000 cm⁻¹ to analyze the incorporation of different functional groups in the LLPPI crystal. The recorded FT-IR spectrum is shown in Fig. 3. The functional groups corresponding to the methyl, amino and carboxyl functional groups were assigned to the peaks at 2961 cm⁻¹, 1503 cm⁻¹ and 1583 cm⁻¹, respectively, which are the characteristic IR peaks of L-leucine. The strong absorption peak at 1685 cm^{-1} of the phthalic acid, which is an aromatic carboxylic acid, is assigned to the C=O stretching vibrations. The peaks at 1278 cm^{-1} and 1065 cm^{-1} are due to C-O stretching and O-H bending of the carboxylic acid, respectively. Further, the combination of NH₃⁺ bending vibrations are assigned to the peaks at 2646 cm^{-1} and 2523 cm⁻¹. Symmetric stretching of the COO⁻ observed at 1402 cm⁻¹ appeared at 1407 cm⁻¹ in pure L-leucine [8]. All these functional groups and bond vibrations confirm the formation of the LLPPI compound.



Fig. 3. FT-IR of LLPPI.

3.4. Optical absorption studies

The optical absorption spectrum of the grown crystal was recorded using Varian Cary 5E spectrophotometer in the wavelength range of 200 to 1400 nm. The recorded spectrum is shown in Fig. 4. From the spectrum it is clear that there is no absorption of light in the entire visible region. The widened transparency is observed in the region of 225 nm to 1400 nm. The lower cutoff wavelength is found to be around 227 nm. The UV cutoff wavelength of some of the L-leucine family crystals is listed in Table 1 and it is observed that LLPI has wider transparency compared to L-leucinium, L-leucinium picrate and L-leucine nitrate. The transmittance of both fundamental (1064 nm) and second harmonic (532 nm) waves can be achieved, hence, the LLPPI compound can be a suitable material for NLO device fabrication.



Fig. 4. UV-Vis absorption spectra for LLPPI crystal.

The optical energy band gap of the crystal is determined from the transmittance spectra using the relation:

$$\alpha h \gamma = Q (h \gamma - E_g)^n \tag{1}$$

where Q is a constant which varies with transitions, h is the Plank's constant, γ is the frequency of the photon, E_g is the band gap of the material and n is an index which can have the values 1/2, 1/3, 2 or 3 depending on the nature of the electronic transitions. Here, the value of n is considered as 1/2 for an allowed direct transition. The optical absorption coefficient α is calculated from the equation:

$$\alpha = \frac{Abs}{d} \tag{2}$$

where Abs is the absorbance and d is the thickness of the crystal. The energy gap (E_g) is calculated from the graph of $(\alpha h \gamma)^2$ versus energy h γ (Fig. 5) by extrapolation of the linear part. The calculated band gap was found to be 5.4 eV, which indicates that the crystal has large photon absorption for harmonic generation.

Compound	UV cutoff wavelength in nm
L-leucine	220 [8]
L-leucinium L-leucinium picrate	480 [12]
L-leucine phathalic acid potassium iodie	227*
L-leucine nitrate	310 [9]

Table 1. UV cutoff wavelength of the reported L-leucine family crystals.

*Present work



Fig. 5. Graph of $(\alpha h \gamma)^2$ versus energy $h \gamma$.

3.5. Thermal analysis

In order to reveal the thermal properties of the title compound, thermogravimetric analysis (TGA) was carried out using simultaneous thermal analyzer PL-STA 1500. The resulting thermogram is shown in Fig. 6. The initial mass of the sample taken to carry out the experiment was 4.3 g. The TGA curve clearly shows two stages of decomposition. Initially there is no weight loss up to 160 °C and the material starts to dissociate at 160 °C and the process continues up to 200 °C. The sudden weight loss between 160 °C and 200 °C is due to dissociation of L-leucine [8]. The second decomposition occurs in between 210 °C to 250 °C. The peak observed at 192 °C represents the melting point of the grown crystal and another peak observed at 244 °C indicates the decomposition of the additives in the crystal. Further, the dissociation happening between 260 °C to 340 °C probably accounts for the evolution of some gases, like nitrogen, ammonia, etc. The absence of endothermic or exothermic peaks indicates that there is no phase transition before the decomposition point. Thus, from thermal analysis it may be noted that LLPPI is stable and can be utilized for device application up to 192 °C. Some of the reported thermal stability data of the L-leucine family crystals is depicted in Table 2. It is observed that the grown crystal has better stability than L-leucine nitrate.



Fig. 6. TG-DTA of LLPPI.

3.6. EDAX analysis

Energy dispersive X-ray analysis (EDAX) was performed using FEI QUANTA 200F spectrometer to obtain the crystalline information of the grown crystal. Specially, this technique is very useful for both qualitative and quantitative determination of elements present in a sample. A fine beam of Xrays was made to fall on the sample and the energy of X-rays emitted by the sample was measured by an energy-dispersive spectrometer. Since the energy of the X-rays emitted from the sample is attributed to the energy difference between the two shells of the atomic structure of the compound, the

Crystals	Thermal stability in °C
L-Leucine	268 [8]
L-Leucinium oxalate	203 [10]
L-Leucine L-leucinium picrate	195 [12]
L-Leucine phathalic acid potassium iodide	192*
L-Leucine nitrate	159.7 [<mark>9</mark>]
*Present work	

Table 2. Thermal stability of some of the reported L-Leucine family crystals.

elemental composition of the sample can be measured. The obtained EDAX spectrum and Table 3 show the close agreement between the experimental and theoretical weight percentages of elements (C, N and O) which confirms the formation of the title compound. Fig. 7 shows the EDAX spectrum of LLPPI.



Fig. 7. EDAX spectrum of LLPPI.

3.7. SEM studies

In order to study the nature and surface morphology of the LLPPI crystal, SEM analysis has been employed. The recorded SEM image is shown in Fig. 8. A two dimensional image was generated over a selected area of the sample. Since LLPPI is a semi-organic crystal, which is poor conducting in nature, the sample was subjected to gold/carbon coating. From the figure it is clear that the crystal possesses almost smooth and free from cracks surface. However, a few microcrystals are seen on the surface. This may be due to the impact of the growth conditions.



Fig. 8. SEM image of LLPPI crystal.

3.8. Dielectric studies

The dielectric constant (ε_r) and dielectric loss (tan δ) of the LLPPI crystal were measured using HIOKI 352-50 LCR HITESTER instrument by a conventional parallel plate capacitor method. Silver coating was applied on the opposite faces of the crystal which was then placed between two copper electrodes. The capacitance was measured for various frequencies in the range of 100 Hz to 5 MHz at room temperature. Further, the value of dielectric constant was calculated using the relation:

$$\varepsilon_r = Ct/\varepsilon_o A \tag{3}$$

where C is capacitance, t is thickness of the sample, ε_0 is permittivity of free space and A is the area of cross section. The variation of ε_r with applied frequency is shown in Fig. 9.

Element	Weight % (Experimental)	Weight % (Theoretical)
СК	55.75	56.57
4.58	4.71	
O K	31.22	32.32

Table 3. EDAX quantification table.



Fig. 9. Variation of dielectric constant with frequency.

It is seen that the dielectric constant is high at low frequencies due to the predominance of electronic, ionic, dipolar and space charge polarisation. However, the dielectric constant value decreases with an increase in frequency and attains a constant value at high frequency region. This constant value being independent of frequency is due to the fact that on increasing frequncy the polarization mechanisms are deactivated one after the other as they are unable to act in accordance with the change in electric field. At higer frequencies (10^{15} Hz) electronic or interfacial polarization has a significant contribution. Further, Fig. 10 shows a dependence of dielectric loss on frequency. It is clear that dielectric loss also decreases with increasing frequency similar to dielectric constant. The property of lower dielectric loss at higher frequency suggests that the grown crystal has a good optical quality with fewer defects. This parameter is of vital importance for NLO materials in their applications. The nature of decreasing of dielectric constant and dielectric loss with frequency suggests that the grown crystal seems to contain dipoles of continuously varying relaxation times. As the dipoles of larger relaxation times are not able to respond to the higher frequecies, the dielectric constant and dielectric loss are low. The materials which have lower dielectric constant and dielectric loss at higher frequencies find important applications in the construction of electrooptic devices [17–19].



Fig. 10. Variation of dielectric loss with frequency.

The AC condctivity as a function of applied frequency was also measured using the relation:

$$\sigma_{ac} = \varepsilon_r \varepsilon_o \omega \tan \delta \tag{4}$$

where ε_0 and ω are permittivity of free space and the angular frequency ($\omega = 2\pi\nu$) of the applied field, respectively. The observed variation is shown in Fig. 11. It is seen that the conductivity increases with an increase in the frequency. This nature is attributed to the reduction in the interfacial polarization at higher frequencies.

3.9. Hardness studies

Hardness is one of the mechanical properties which gives the information about the molecular



Fig. 11. Frequency dependence of AC conductivity.

binding, yield strength and elastic constants of a material. The Vickers microhardness values were estimated by SHIMADZU HMV-2T microhardness tester for different loads on the polished face of LLPPI crystal. Vickers hardness number (H_V) was calculated using the relation:

$$H_V = 1.8544(P/d^2) \text{kg/mm}^2$$
 (5)

where P is the applied load and d is the diagonal length of the indentation impression. The microhardness profile is shown in Fig. 12a. It is observed that the hardness of the crystal increases with the applied load. The higher hardness value of crystal appears to be due to absence of liquid inclusions and higher stress required to form dislocations.

The Mayer's index n for the grown crystal was calculated from Mayer's equation [20] which is given by $P = K \cdot d^n$ or $logP = logK + n \cdot logd$, where K is the material constant. The above relation shows that H_V should increase with load if n > 2 and decrease with load when n < 2. According to Onitsch [21] the value of n should lie between 1 to 1.6 for hard materials and for soft materials it should be above 1.6. The graph was plotted as log p against log d to calculate the value of n. The resulting graph is shown in Fig. 12b. The calculated n value of the LLPPI crystal is found to be greater than 1.6. Therefore, it belongs to soft material category.



Fig. 12. (a) Variation of hardness with load; (b) plot of logP against logd.

3.10. SHG efficiency measurements

As LLPPI crystallized in is nonа centrosymmetric space group, a preliminary study of the powder SHG conversion efficiency was also carried out using the Kurtz and Perry method [22]. A Q-switched Nd:Yag laser beam of a wavelength 1064 nm was used with an input power of 2.4 mJ/pulse, pulse width of 10 ns and the repetition rate being 10 Hz. The crystals were ground to a uniform particle size of about 125 to 150 µm and then packed in a capillary of uniform bore and exposed to the laser radiation. The powders of KDP and urea with the same particle size were used as the reference. The emission of green radiation of wavelength 532 nm from the crystal confirms the SHG generation in the crystal. From the crystalline sample, it was found that the efficiency of second harmonic generation (26 mV) is found to be 0.76 and 0.32 times that of pure KDP (34 mV) and urea (81 mV), respectively.

4. Conclusions

Single crystals LLPPI have been grown by slow evaporation technique from aqueous solution. Single crystal X-ray diffraction analysis confirmed the crystal system and lattice parameters. The functional groups present in the title compound were confirmed by FT-IR analysis. Optical absorption studies showed the transparency of the crystal in the visible and ultraviolet regions. Thermal studies revealed that the title compound is stable up to 192 °C. EDAX studies confirmed the formation of the new compound and surface analysis showed that the grown crystals possessed smooth surface. Dielectric studies revealed that the dielectric constant decreased with an increase in frequency. The powder Kurtz method was used to study the SHG efficiency of the grown crystals and the conversion efficiency was found to be 75 % and 30 % of pure KDP and urea, respectively.

Acknowledgements

The scientific supports extended by STIC, Cochin University, Kerala and Department of IPC, IISC, Bangalore are gratefully acknowledged.

References

- [1] SASAKI T., YOKOTANI A., J. Cryst. Growth, 99 (1990), 820.
- [2] ADACHI H., TAKAHASHI Y., YABUZAKI J., MORI Y., SASA T., J. Cryst. Growth, 198 (1999), 568.

- [3] PRASAD P.N., WILLIAMS D.J., Introduction to Nonlinear Optical Effects in Organic Molecules and Polymers, Wiley, New York, 1991.
- [4] BABU D.R., JAYARAMAN D., KUMAR R.M., RAVI G., JAYAVEL R., J. Cryst. Growth, 250 (2003), 157.
- [5] KALAISELVI D., JAYAVEL R., Appl. Phys. A-Mater., 107 (2012), 93.
- [6] CHAROEN-IN U., RAMASAMY P., MANYUM P., J. Cryst. Growth, 362 (2013), 220.
- [7] KUMAR R.M., BABU D.R., JAYARAMAN D., JAYAVEL J., KITAMURA K., J. Cryst. Growth, 275 (2005), 1935.
- [8] ADHIKARI S., KAR T., *Mater. Chem. Phys.*, 133 (2012), 1055.
- [9] ADHIKARI S., KAR T., J. Cryst. Growth, 356 (2012), 4.
- [10] ANBUVHEZHIYAN M., PONNISAMY S., MUTHAMIZHCHELVAN C., Optoelectron. Adv. Mat., 3 (2009), 1161.
- [11] MARCHEWKA M.K., DROZD M., Cent. Eur. J. Chem., 11 (B) (2013), 1264.
- [12] BHAGAVANNARAYANA G., RISCOB B., SHAKIR M., Mater. Chem. Phys., 126 (2011), 20.
- [13] KUMAR A.S., RAMASAMY P., VERMA S., J. Cryst. Growth, 318 (2011), 757.
- [14] BECK L., STEMMLER P., LEGRAND F., Rev. Sci. Instrum., 66 (1995), 1601.
- [15] GOEL N., KUMAR B., J. Cryst. Growth, 361 (2012), 44.
- [16] BENEDICT J.B., WALLACE P.M., REID P.J., JANG S.H., KAHR B., Adv. Mater., 15 (2003), 1068.
- [17] HARAMI T., YAMAGISHI E., OKUDA A., Jpn. J. Appl. Phys., 13 (1974), 924.
- [18] HUNDELSHAUSHEN VAN U., *Phys. Lett. A*, 34 (1971), 405.
- [19] JAGADEESH M.R., SURESH KUMAR H.M., ANANDA KUMARI R., Arch. Appl. Sci. Res., 6 (4) (2014), 188.
- [20] JAGANNATHAN K., KALAINATHAN S., NARAYANA G. B., *Mater. Lett.*, 61 (2007), 4485.
- [21] ONITSCH E.M., Mikroskopie, 2 (1947), 131.
- [22] KURTZ S.K., PERRY T.T., J. Appl. Phys., 39 (1968), 3798.

Received 2014-10-14 Accepted 2015-03-27