GROWTH AND CHARACTERIZATIONOF POTASSIUM CHLORIDE AND POTASSIUM IODIDE DOPED AMINO ACIDNLO SINGLE CRYSTALS

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Single crystals of potassium chloride and potassium iodide doped L Alanine were grown by slow evaporation process. The grown compounds were characterized by powder XRD analysis to confirm the crystalline nature. The cell parameters and structure of grown crystals were identified through single crystal XRD analysis. FTIR and UV–visible spectra revealed the presence of functional groups and optical property of the grown crystals respectively. The mechanical property of the grown crystals was determined by Vicker's micro hardness test. Thermo gravimetric analysis (TGA) was performed to study the thermal stability of the grown crystals.

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1. Introduction

In the current decades, there has been a growing interest in crystal growth process, particularly in view of the development of materials for technological applications[1]. Non – linear optical materials (NLO) have wide applications in the area of laser technology, optical communication and in storage technology. Several important technologies like microelectronics,optoelectronics, computers, photonics, lasers, information science, etc., need well characterized bulk single crystals. In recent years the amino acid group materials were mixed with organic or inorganic salts in order to improve their chemical stability, laser damage threshold, thermal and physical properties and non-linear optical properties. Amino acids are interesting organic materials for NLO applications. They contain proton donor carboxylic acid (COOH) and the proton acceptor amino (NH_2) groups which provide the ground state charge asymmetry of the molecule required for second order non linearity[2,3]. L-alanine is an essential amino acid with the chemical formula CH_3CHNH_2COOH and it is an important source of energy for muscle tissue, the brain and central nervous system and also it strengthens the immune system by producing antibodies, helps in the metabolism of organic acids and sugar. Organic - inorganic hybrid materials have attracted considerable attention[4]. Therefore they are potential candidates for optical second harmonic generation. In this present work, to enhance the properties of L alanine single crystals, potassium chloride and potassium iodide were used as dopants. The growth of single crystals of potassium chloride doped L alanine (LAPC) and potassium iodide doped L alanine (LAPI) had been carried out by slow evaporation technique. The grown crystals were analyzed through various characterization techniques.

2. Experimental Procedure

High purity (99.9% AR grade) samples of L alanine, potassium chloride and potassium iodide were used for the crystal preparation. The saturated solutions of L alanine and potassium chloride were prepared using doubly distilled water as a solvent using magnetic stirrer. Both the solutions were mixed in the ratio of 1:3. Similarlythe saturated solution of potassium iodide was

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prepared. The prepared saturated solutions of L alanine and potassium iodide were also mixed in the ratio 1:3. The above solutions were taken in two separate beakers and kept in magnetic stirrer and are allowed to stir for four hours to get a good homogeneity of the mixers. Being stirred well the solutions were filtered using WhatmanNo.1 filter paper to remove the impurities. The filtered clear solutions of potassium chloride doped L alanine with pH value 6 and potassium iodide doped L Alaninewith pH value 6 were taken in well cleaned beakers, covered with Aluminum foil sheets with pours in order to favour slow evaporation process. The beakers with filtered solutions were kept in a dust free and vibration free environment and allowed to crystallize. The grown crystals LAPC and LAPI were harvested after the time period of 50 days and 28 days with the dimension of 13x12x5 mm^3 and 11x7x4 mm^3 respectively. The photographs of the grown crystals were shown in figs. 1a and 1b.

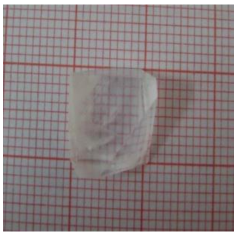


Fig. 1a. Photograph of LAPC

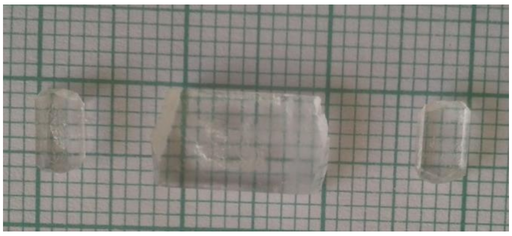


Fig. 1b Photograph of LAPI

3. Characterization

A complete description of the physical and chemical properties of a material of interest is termed as characterization of that material. This helps to study the growth process and to improve the quality of the crystal[4]. The grown crystals LAPC and LAPI were subjected to powder and single XRD analysis, FTIR, UV-Vis, hardness measurement and TGA studies.

4. Results and Discussion

4.1 Powder XRD analysis

X-ray diffraction technique is a powerful tool to analyze the crystalline nature of the materials. If the material to be investigated is crystalline, well defined peaks will be observed[5,6,]. In our present work the grown crystals were subjected to powder X-ray diffraction analysis. The powder X-ray spectra was recorded using SEIFERT X-ray diffractometer with CuKα Radiation (λ =1.5406).

The powdered sample was scanned over the range of 10 to 80 degrees. The peaks in the diffractogram were indexed. The XRD pattern of the grown crystal of LAPC and LAPI were shown in the figs. 2a and 2b. The presence of number of good intensity and sharp peaks prove the crystalline nature of the grown crystals. It is observed that in both LAPC and LAPI single crystals; there is a variation in intensity and shift in position of peaks compared to the peaks of L alanine.

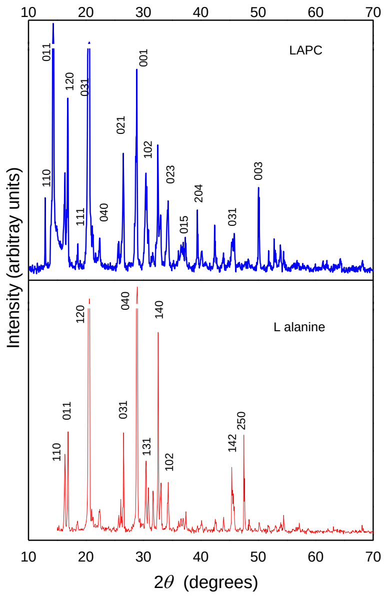


Fig. 2a. Powder XRD pattern of LAPC

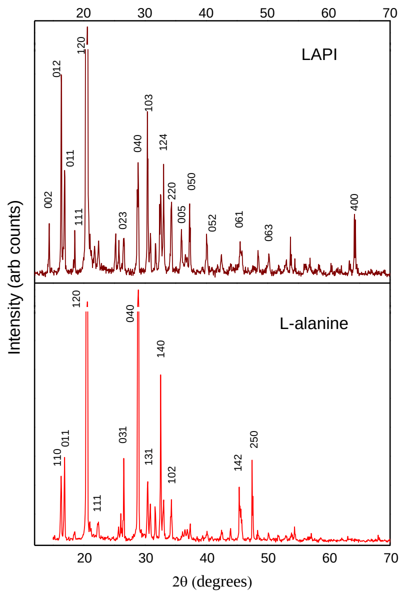


Fig. 2b. Powder XRD pattern of LAPI

4.2. Single XRD analysis

The grown crystals had been subjected to single crystal XRD employing a Bruker AXS diffractometer using MoKα radiation (λ = 0.71073Å). The single crystal XRD revealed that the crystals of LAPC and LAPI belong to orthorhombic system. The lattice parameter values were compared in Table 1. The results of the present work were in good agreement with the reported values[3]. The grown crystal LAPC posses the same crystal system as that of L alanine that is orthorhombic and space group $P2_12_12_1$.

Table 1. Cell parameters of the grown crystals using SXRD

Crystal	a(A^0)	b(A^0)	c(A^0)	α=β= γ	Cell Volume (A^{03})	Space group	Crystal system
L Alanine	6.023	12.343	5.784	90^0	429.541	$P2_12_12_1$	Orthorhombic
LAPC	6.0321	12.3395	5.7792	90^0	430.134	$P2_12_12_1$	Orthorhombic
LAPI	12.0585	12.3258	5.7794	90^0	858.996	$P2_1/m$	Orthorhombic

The crystal system of LAPI was also identified as Orthorhombic but the space group has been changed as $P2_1/m$ which is considered to be an evidence for the dopant's inclusion with the parent. It was identified that there is change in the values of lattice constants there by increasing the cell volume. The single XRD analysis confirmed that the doping of potassium derivatives (KCl and KI) does not alter the basic structural properties of L alanine crystal[7].

4.3. FTIR analysis

Vibrational spectroscopy is useful in the identification of functional groups. Infrared radiation, when incident upon matter is capable of giving indirect but very valuable information on molecular structure. Band assignments have been made in analogy with various functional groups like amino acids, carboxylic acids etc**.** The FT-IR spectrum of the grown crystals were recorded in the region 4000-400 cm^{-1} employing Shimadzu IFS and are shown in the figures 3.a and 3.b.

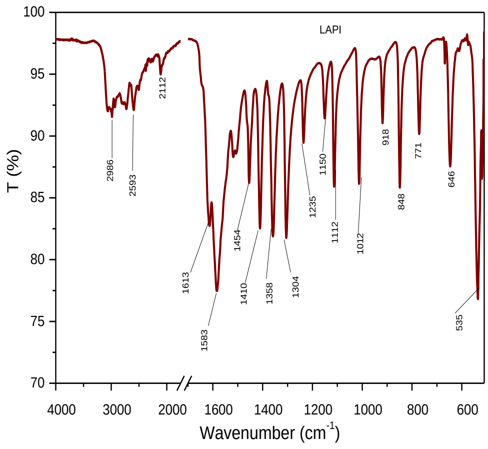


Fig.3a. FTIR spectrum of LAPC

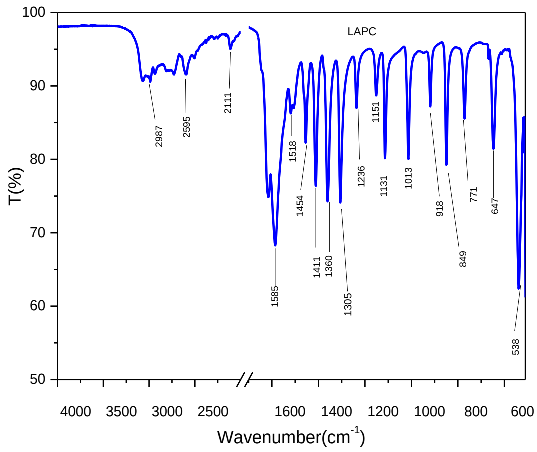


Fig.3b. FTIR spectrum of LAPI

From the figures, various absorption peaks present in the recorded FTIR spectra of the grown crystals were assigned to their corresponding functional groups and are listed in table.2[2]. The functional groups corresponding to L alanine were confirmed in both the grown crystals at almost same frequency ranges[3,4,8]. The presence of chlorine in LAPC crystal was confirmed by C-Cl stretching[9] at 538 cm^{-1}. Similarly the presence iodine is realized by the peaks at 731 cm^{-1} and 536 cm^{-1} in the LAPI crystal.

Table 2. FTIR spectral data of grown crystals

Band assignment	Wave number in cm^{-1}	
	LAPC	LAPI
O-H stretching	2987,2595	2986,2593,1112
Overtones and combination bands with prominent peaks near 2500 and 2000 cm-1	2111	2112
C=O stretching	1585	1613,1583
C-H in plane bending	1454,1411	1454,1410
C-H symmetric stretching	1305	1304
C-O-C stretching	1236,1151	1235
C-N	1131	
C-CHO stretching	1013	1012
O-H bending(out of plane)	918	918
C-H out of plane bending	849,771,647	848,646
C-Cl stretching	538	
C-I stretching		731,536

4.4 UV–visible spectral studies

The single crystals are mainly used for optical applications. The optical transmittance range and transparency cut off are important for any crystal. The UV–visible study of LAPC and LAPI crystals were carried out by Lambda 35 model UV–visible spectrometer in the spectral range 200–1100 nm. The transmission spectra of grown crystals are shown in Figs. 4.

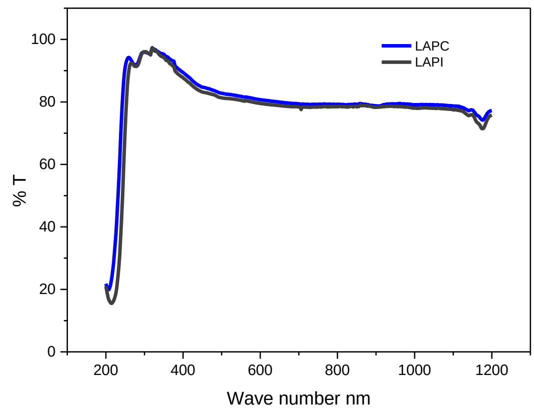


Fig.4. UV-Vis spectra of LAPC and LAPI

From the spectra it is clear that the lower cutoff value of L APC is 246 nm and that of L-LAPI is 261 nm. The percentage of transmittance of grown crystals is 83.6 for LAPC and 81 for LAPI respectively. This property of the grown crystals can be utilized in the field of NLO[10].

4.5. Micro hardness

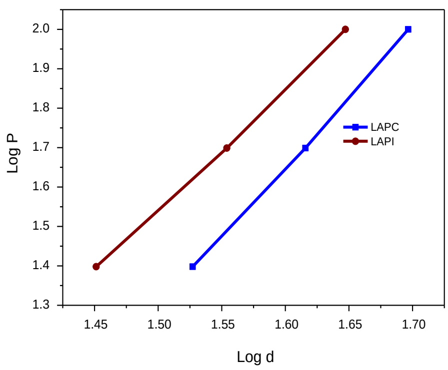
The resistance offered by a material to the motion of dislocation, deformation or damage under an applied stress is measured by the hardness of the crystal. During the making of NLO crystals mechanical stress is applied on the crystal while cutting and polishing. So it is necessary to know the mechanical stress the crystals can withstand without any crack. The ratio of the applied load to the projected area of indentation gives the hardness.

The mechanical characterization of the grown crystals had been done by micro hardness testing at room temperature. Transparent crystals free from cracks, with flat and smooth faces, were chosen for the static indentation tests. Now the selected faces had been indented gently by the loads varying from 25 to 100 g for a dwell period of 10 s using Vicker's diamond pyramid indenter attached to an optical microscope.

The Vickers hardness number (Hv) was calculated using the standard formula,

$$H_V = 1.8544\frac{P}{d^2}$$

where P is the applied load and d is the mean diagonal length of the indentation.



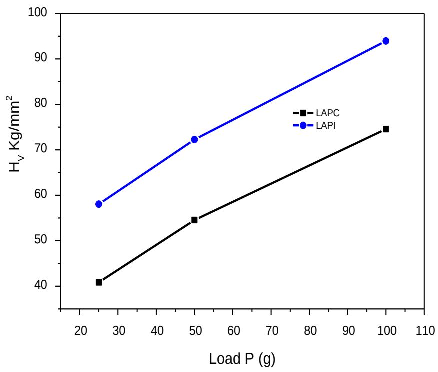


Fig. 5a Load P Vs H_V of LAPC

Fig.5b log d Vs log P of LAPI

From the figure 5a, drawn between load P and Hardness number H_V, the hardness value increased with the increasing load and hence the grown crystals exhibited the reverse indentation size effect (RISE)[11]. According to the Meyer's law, the relation between the load and size of indentation is $P=k_1d^n$, where 'k_1' is the material constant, 'n' is the Meyer's index or work hardening coefficient. The above relation shows that H_V should increase with load if $n > 2$ and decrease with load when $n < 2$. The plot of log P against log d is shown in figure 5b, which gave a straight line (after least square fitting). The slope of the line, (n, the Meyer's index) for the grown crystal LAPC was 3.375 and that for LAPI was 3.12. According to Onitsch and Hanneman, 'n' should lie between 1 and 1.6 for hard materials and should be above 1.6 for soft materials and hence both the grown crystals belonged to soft material category. The higher hardness value of crystal appeared to be due to the absence of liquid inclusions[12].

Table 3. Variation of Hardness number and stiffness constant with load

Sample	**Load P (g)**	**Hardness number H_V**	**Stiffness constant C_{11} (x10^{14}Pa)**
L Alanine	25	38.5	5.95
	50	50.4	9.53
	100	61.55	13.5
LAPC	25	40.85	6.600
	50	54.55	10.949
	100	74.55	19.003
LAPI	25	58.05	12.208
	50	72.25	17.904
	100	93.95	28.35

Elastic stiffness constant (C_{11}) was calculated by Wooster's empirical relation as

$$C_{11} = H_V^{7/4}$$

Stiffness constant for different loads calculated from Vickers hardness values are given in table 3. From the table, it was clear that the stiffness constant increased with increase in load. Hence the high value of C_{11} indicated that the binding forces between the ions were quite strong[11, 13-15].

Hence it was confirmed that the mechanical properties like Mayer's index and stiffness constant had increased considerably for the grown crystals LAPC and LAPI compared to pure L alanine single crystals due to doping. This increase in the hardness of doped crystals can be attributed due to the incorporation of impurities in the lattice of L alanine. It is in good agreement with theoretical prediction[16].

4.6 Thermal studies

The thermal behavior of the grown crystals was studied by TGA, recorded using PerkinElmer Diamond instrument. An alumina crucible was used for heating the sample and analyses were carried out in an atmosphere of nitrogen at a heating rate of 10°C/min in the temperature range of 20–700°C. The TGA curves of LAPC and LAPI are shown in Fig. 6a and 6b, which explained the decomposition and percentage of weight loss of the grown crystals at various temperatures.

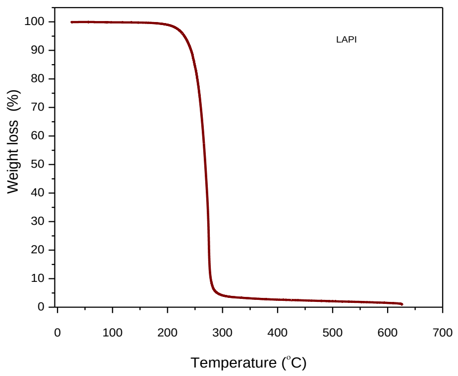


Fig.6a TGA curve of LAPC

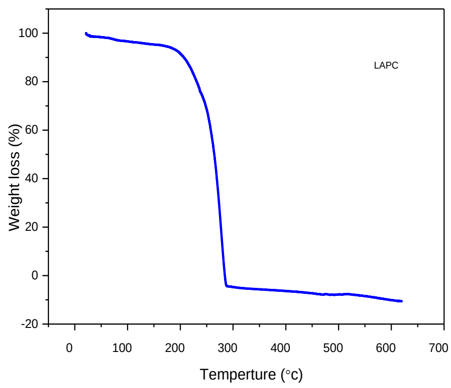


Fig.6b TGA curve of LAPI

For the crystal LAPC, there was a single major weight loss started at about 192°C. Below 192°C there was no detectable weight loss as there was no decomposition up to melting point which showed the rejection of solvent molecules by the crystal during crystallization. The sharp weight loss at 192°C without any intermediate stage was assigned as the decomposition point of the crystal. The total weight loss (100%) had occurred at the temperature of 289°C.From the graph, the melting point of LAPC was found to be 192°C

TGA curve of LAPI crystal also took a similar variation as LAPC crystal. Sharp and single weight loss started at the temperature of 207°C and ended at 281°C with a decomposition of 94% of the sample. The remaining 6% of the sample was stable upto700°C. So the melting point of the crystal LAPI was found to be 207°C.

The TGA of LAPC and LAPI were indicative of the good thermal stability of the grown crystals. Another important observation was that, there was no phase transition and color change till the materials melted and this enhances the temperature range for the utility of the crystal for NLO applications[17-19]. Since LAPC and LAPI crystals can retain texture up to 192°C and 207°C respectively, it is better than the other semi-organic materials like L alanine cadmium chloride (110°C), triallylthiourea cadmium chloride (101°C), triallylthiourea cadmium bromide (97°C), triallylthiourea mercury chloride (133°C) and allyl thiourea mercury bromide (125°C)[20-22].

5. Conclusion

Good quality, transparent, single crystals of potassium derivatives doped L alanine (LAPC AND LAPI) were successfully grown by slow evaporation method. The grown crystals were analyzed using powder XRD analysis which confirmed the crystalline nature. The FTIR analysis clearly indicates the functional groups present in the crystal by their corresponding characteristic peaks. The optical transmission study revealed the lower cut off wavelength as 246 and 261 nm, for LAPC and LAPI respectively. This is to ascertain the fact that the crystals can be used for laser applications and device fabrication. From the Micro hardness analysis it was identified that the hardness number and stiffness constant had increased with increase in load for the grown crystals LAPC and LAPI. The Meyer's index values reveal that the grown crystals belong to soft material category. The thermal studies confirmed that the grown crystals LAPC and LAPI were stable up to 192°C and 207°C respectively and indicate its suitability for applications in laser field. From the above studies, it is concluded that due to these improved properties, these crystals find its potential applications in the areas of device fabrication, laser technology, and optical communication and in storage devices.

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