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Growth and Spectral Studies of Unidirectionally grown L-Threonine Acetate single crystal

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ABSTRACT

Unidirectional <110> bulk L-Threonine acetate (LTA) single crystal was successfully grown for the first time by Sankaranarayan–Ramasamy (SR) method. The <110> oriented plane have been placed as seed at the bottom of the ampoule and a transparent single crystal of LTA of 10 mm diameter and 50 mm length have been grown. The crystal system and lattice parameters were analyzed from the single crystal x-ray diffraction study. FT-IR and FT-Raman analyses were used to confirm the presence of the functional groups. The grown crystal was also characterized by UV-Vis-NIR absorption and micro hardness. The second harmonic generation (SHG) in the sample was confirmed by Kurtz and Perry powder technique. The laser damage threshold was also found.

Key words: Crystal growth; Characterization methods; Optical materials and properties.

INTRODUCTION

Amino acids and its complexes belong to a family of organic materials which are also used in photonics based fabrications. Organic crystals show high damage threshold, wide transparency region and non-linear optical character which make them suitable for device fabrication [1 - 3]. In experimental solid state physics, SR method is a novel technique and used for the growth of unidirectional LTA single crystal [4]. It is also a convenient method used significantly to control the orientation of the growth of single crystals. Recently L-Threonine acetate single crystals were reported as promising nonlinear optical material [5]. In the present study, large size unidirectional single crystal of LTA was grown successfully by the SR method for the first time. The techniques like single XRD, UV-Vis-NIR, FT-IR, FT-Raman and micro hardness were selected to characterize the grown crystal.

MATERIALS AND METHODS

The experimental setup of SR method consists of growth ampoule made-up of glass with seed mounting pad. The circular shaped heaters were placed at the top and the bottom of the growth ampoule which provides the required experimental temperature for solvent evaporation [4]. The temperature around the growth ampoule is selected based on the solvent used and it is monitored with a temperature controller (40ºC for top and 34ºC for bottom). The seed crystal from the conventional slow solvent evaporation technique was used for the current study. <110> plane of the seed crystal of LTA was chosen and it was transferred to the saturated solution of LTA. The chemical reaction involved for the grown L-Threonine acetate is given below:

$$C_4H_9NO_3 + CH_3COOH \rightarrow C_4H_{10}NO_3^{+}\ CH_3COO^{-}$$

Growth of highly transparent single crystal of LTA of 10mm diameter and 44 mm length was harvested (Figure.1.) in a period of 30 days and reported for the first time. The average growth rate was found to be nearly 1.5 mm per day. From this, it was depicted that the average growth rate of crystal by SR method was higher than the conventional method under prevailing conditions.

RESULTS AND DISCUSSION

3.1 Single Crystal XRD

The experimentally grown crystal was subjected to single crystal X-ray diffraction study using ENRAF NONIUS CAD F4 diffractometer. LTA Single crystal belongs to orthorhombic crystal system with a space group $P2_12_12_1$ and unit cell dimensions were found to be a = 5.542Å, b = 8.131Å, c = 13.912Å. The volume of the system is V=626.903Å^3. From the above values, it is evident that the unit cell parameters agree well with the reported values [5].

3.2 FT- Raman spectrum

In order to qualitatively analyze the presence of functional groups in LTA, Fourier Transform Raman (FT-Raman) spectrum was recorded in the range 500 cm^{-1} – 3500 cm^{-1}. The FRA 106 module attached to IFS 66V FT-IR spectrometer provided the FT-Raman spectral measurements. The recorded FT-Raman spectrum of LTA is shown in Figure 2. The O-H stretching is illustrated by a peak at 2988 cm^{-1} in the Raman Spectra. The bands at 2938 cm^{-1} and 2873 cm^{-1} are due to aliphatic CH_2 and CH_3 stretching. The less intense peak at 1481 is due to the CH_2 deformation. The peak at 1337 cm^{-1} is due to the C=O stretching. The weak absorption at 3100 cm^{-1} is due to the N-H stretching of amino group.

3.3 FT- IR spectrum

Freshly crushed powders of pure and doped were mixed respectively with KBr in the ratio 1:10 and pelletized using a hydraulic press and subjected to the Fourier Transform Infrared (FT-IR) studies. The spectra were recorded in the range 500 cm^{-1} – 3500 cm^{-1} employing BRUKER IFS 66V FT-IR spectrometer. The FT-IR Spectrum is shown in Figure 3. The N-H stretching frequencies of amino group are found between 3168 and 2874 cm^{-1} in the IR spectrum. The absorption at 3026 cm^{-1} is due to O-H stretching vibration of carboxylic group. The IR spectrum shows a strong absorption at 1626 cm^{-1} indicates the presence of primary amino group. The

characteristic absorption at 1479 cm^{-1} is due to symmetric N-H deformation. The peak at 1418 cm^{-1} corresponds to the symmetric COO^- stretch. The CH deformation is found by the peak at 1319 cm^{-1}. The wagging of COO^- gives rise to a band at 702 cm^{-1}. The FT-IR spectrum of LTA confirms the structural aspects of the compound.

3.4 UV – Vis – NIR Analysis

The absorption spectra of the directional SR was studied by a Varian Cary 5E spectrophotometer. A crystal of 1mm thickness was used to perform UV–Vis-NIR absorption study (Figure 4.). It was found that the lower UV-cutoff wavelength was 248 nm; hence the crystal can be used for laser applications.

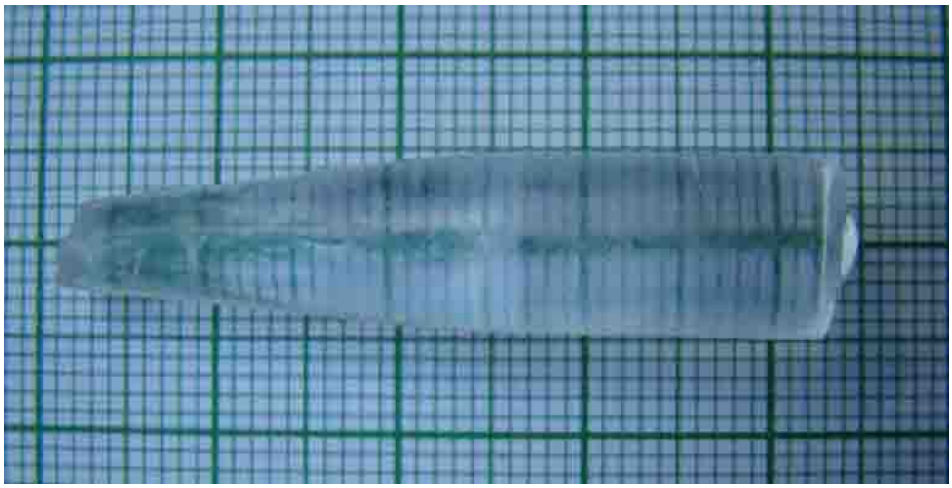

Fig.1.The LTA grown crystal by SR method

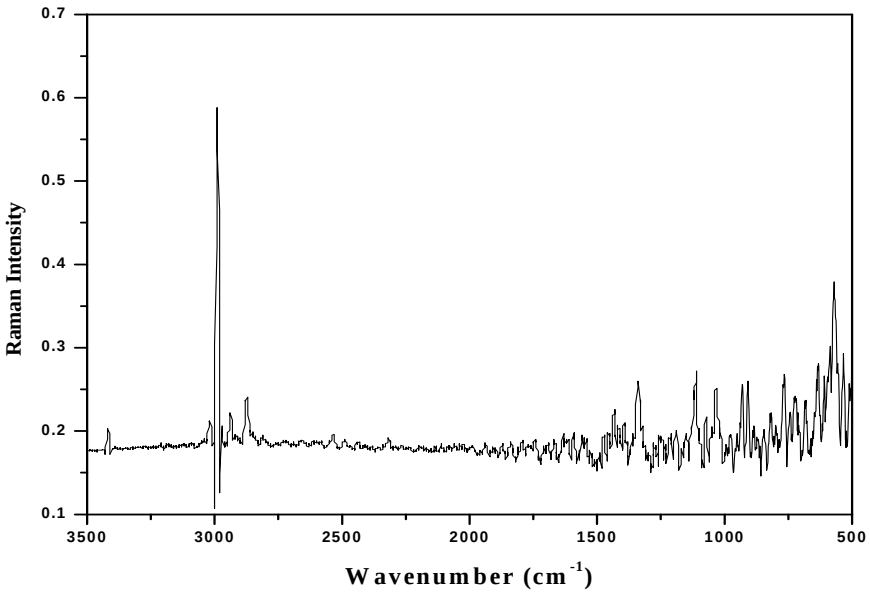

Fig.2. FT- Raman spectrum of LTA single crystal

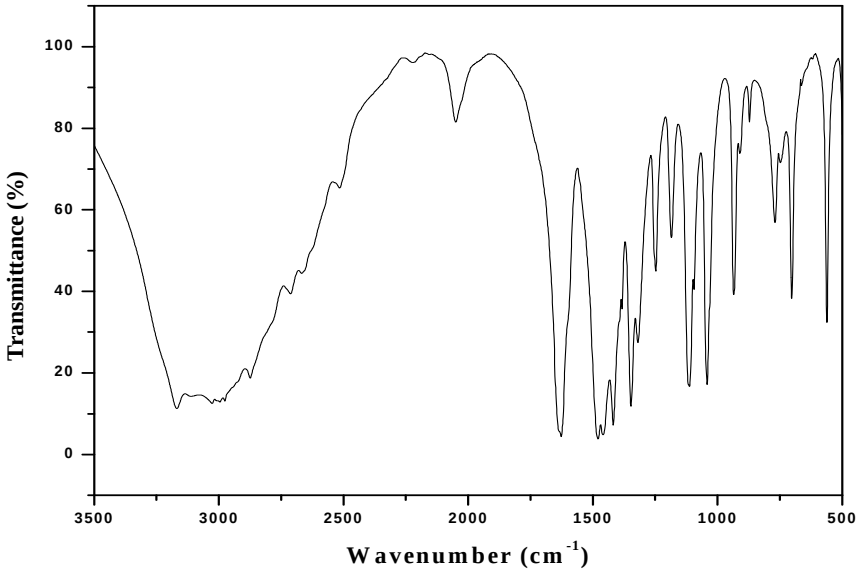

Fig.3. FT-IR spectrum of LTA single crystal

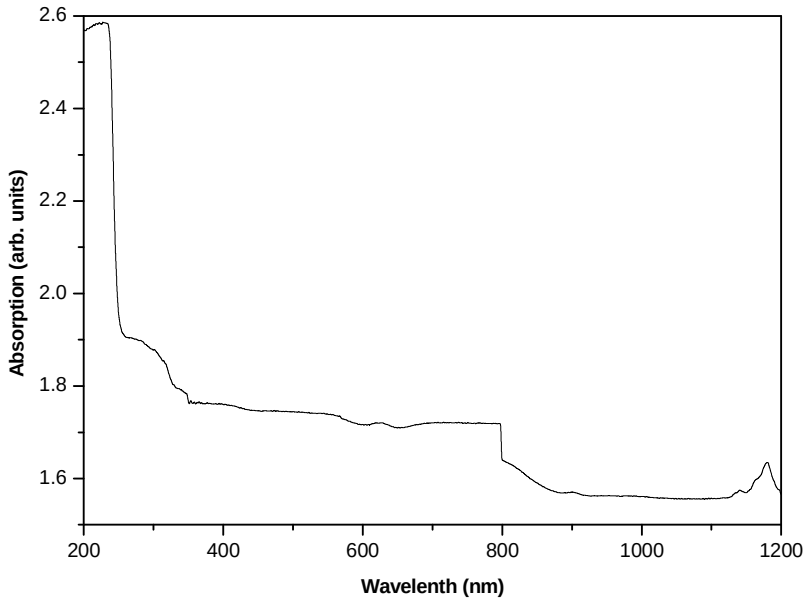

Fig.4. UV - Vis – NIR Absorption Spectrum

3.5 SHG and Laser Damage Threshold

An input pulse of 6.2 mJ was used to illuminate the freshly powdered sample of particle size (above 150 μm). The NLO property of the grown LTA single crystal was analyzed by the Kurtz technique [6]. This study confirmed the green emission of a crystal carried out by SHG test. The quantitative work was done on powdered single crystal of LTA and they were graded by the use of standard sieves to desire the range of particle sizes. A relevant comparison was made on KDP

with LTA. The reference material was also powdered and used for further studies. The experimental samples reported an input pulse of 6.2 mJ, the second harmonic signal (532 nm) of 89.02 mW for KDP and 268.50 mW for LTA. It is thus elucidated that the SHG efficiency of LTA is 3.0 times higher than that of KDP. The suitability of LTA crystal for NLO applications was investigated from laser damage threshold and the value was reported as 8.2 GW/cm^2 using a laser setup in single shot mode.

3.6 Vickers Micro Hardness Study

Vickers micro hardness indentations were made on the LTA crystal at room temperature using a Leitz-Wetzler hardness tester. The micro hardness number, Hv was determined from the relation, Hv = [1.8544 P/d^2] Kg / mm^2, Where *P* is the load in gm, d the diagonal length of the diagonal of the indentation impression in mm and Hv the Vickers hardness in kg/mm^2. A plot was drawn between hardness number and applied load .The hardness number was found to increase with load. It was observed that the hardness value was turn to decrease as load increase (Figure 5) which is in agreement with the normal indentation size effect (ISE) [7].

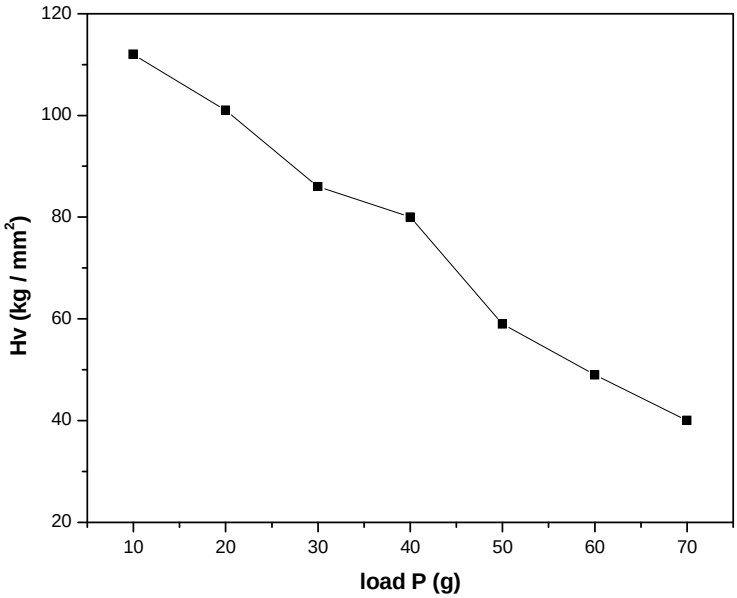

Fig.5. Vickers micro hardness Profile

CONCLUSION

Good quality single crystal of L-Threonine acetate has been grown successfully by the unidirectional solution growth SR method .The lattice parameters were determined from the single crystal XRD and it was shown that it belongs to the orthorhombic crystal system with a space group of $P2_12_12_1$. The FT-IR and FT-Raman spectral studies confirmed the presence of the functional group and their different mode of vibrations. The UV–Vis-NIR absorption study confirms the wide transparency of the SR grown material. Vickers micro hardness was determined to understand the mechanical property of the grown crystal. It was also understood from the present work that the SR technique was found to be suitable method grow high quality and large- size single crystal of L-Threonine acetate.

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