Growth, Mechanical, Optical and Impedance Analysis of Sodium Acetate added L-alanine (SALA) Single Crystals

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***Abstract* — Amino acids are the famous organic materials which can play an important role in nonlinear optics as they contain proton donor carboxylic acid group and the proton acceptor amino group. L-alanine is an organic crystal that belongs to amino acid group composed of optically active material. In this work, sodium acetate added L-alanine single crystals have been grown by solution method with slow evaporation technique for the first time. The cell parameters of the SALA crystal were estimated by X-ray diffraction study. The mechanical properties of SALA crystals were investigated at room temperature using a Vickers hardness tester and various parameters such as work hardening coefficient, stiffness constant, yield strength were evaluated. UV-visible-NIR transmittance spectrum was recorded to study the optical transparency of grown crystal and also the optical band gap of SALA crystal was calculated from the Tauc's plot. The impedance behaviour of the grown crystal was analyzed as a function of frequency.**

Keywords: Sodium acetate, Single crystals, Vickers hardness number, Impedance analysis ,Amono acids

I. INTRODUCTION

Generally, amino acids contain an asymmetric carbon atom and crystallize in noncentro symmetric space group and they are the interesting materials for nonlinear optical and other photonic device applications [1]. L-alanine exists in the cationic form ($C_3H_8NO_2^+$) with a positively charged amino group which crystallizes in an orthorhombic system with space group $P2_12_12_1$ having around one-third second harmonic generation (SHG) efficiency to that of potassium dihydrogen phosphate (KDP) [2]. It is an efficient organic NLO material and considered as the fundamental building block of forming more complex amino acids and it shows strong nonlinear behaviour and abnormal phonon connection [3]. Sodium acetate is an excellent inorganic phase change materials, possesses a high energy storage density and high thermal conductivity [4]. In the present investigation, single crystals of sodium acetate added L-alanine (SALA) have been grown from the mixture of L-alanine and sodium acetate in the aqueous solution by the slow evaporation technique for the first time. In this paper, we present the crystal growth, single crystal X-ray diffraction, optical transmission, microhardness and impedance studies of the SALA single crystals.

II. MATERIAL SYNTHESIS AND CRYSTAL GROWTH

The SALA salt was synthesized by taking AR grade L-alanine and AR grade sodium acetate in the molar ratio of 1:1 and dissolved in double distilled water. The solution was stirred for 2 h using a magnetic stirrer to yield a homogeneous mixture. Then the mixture was evaporated to dryness by heating 45^{o}C and it gives white microcrystalline powder. By repeated re-crystallization, the synthesized SALA salt was well purified and subjected to crystal growth. The saturated aqueous solution of re-crystallized SALA salt was prepared at room temperature and the solution was stirred well using a hot plate magnetic stirrer for 3 h. Then the resulting solution was filtered using 4 micro Whatmann filter paper and it was taken in a crystallizer. Good quality crystals with well-defined morphology were grown by conventional seed immersion technique in CTB at 30^{o}C. A typical single crystal was obtained within a period of 30-35 days and it is shown in the figure 1.

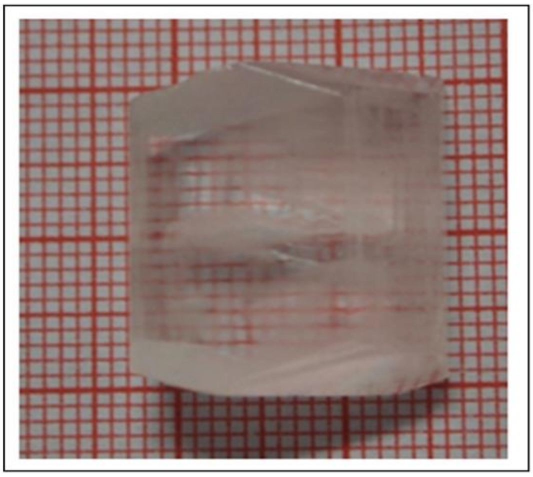

Fig. 1. Photograph of as-grown SALA single crystal

II. RESULTS AND DISCUSSION

A. Structural analysis

The unit cell dimensions of the SALA single crystal were determined by single crystal XRD analysis using ENRAF NONIUS CAD4 diffractometer with Mo K_α radiation. The grown crystal belongs to orthorhombic system with the space group $P2_1 2_1 2_1$. The estimated lattice parameters are a=5.831(7) Å, b=6.050(6) Å, c=12.384(13) Å and cell volume of 436.88 $Å^3$. When compared to the lattice parameters of pure L-alanine [5], the slight changes in the cell parameters of SALA crystal are due to the incorporation of admixtured sodium acetate into the interstitial positions of host crystal.

B. Mechanical strength

Microhardness is the measure of strength of material and is an important mechanical property of the optical materials in the fabrication of devices. The Vickers microhardness method is a well-known technique for measuring the hardness of materials. Microhardness analysis has been carried out carried out using a Shimadzu microhardness tester with a diamond indenter. SALA crystal with flat and smooth face free from any defects has chosen for this static indentation test. Indentations were made on the crystal plane with the various load from 25 to 100 g, by keeping the time of indentation constant (10 s) for all trials at room temperature. At least three indentations have made on SALA sample for each load. The average length of diagonal impression was noted and the Vickers Hardness Number (VHN) has been determined from following the relation [6]

$$H_v = 1.8544\ P/d^2 \qquad (1)$$

where P is the applied load, and d is the average diagonal length of the indenter impression and 1.8544 is a constant of a geometrical factor for the diamond pyramid. The variation of hardness number with load is shown in figure 2, in which the hardness increases with the increase of load. Therefore the grown SALA crystal exhibits the reverse indentation size effect (RISE). For the higher the hardness values, greater is the stress required to form dislocation, thus confirming greater crystalline perfection in SALA crystal. From Meyer's law [7], the relation between load and diagonal length of indentation is

$$P = a\ d^n \qquad (2)$$

where A is a constant and n is the Meyer's index (or work-hardening co-efficient). The value of n is determined from the slope of the plot between ln P versus ln d for the SALA crystal (figure 3). From the graph, the value of n is found to be 4.57. Onitsch and Hannema had shown that the value of n is from1 to 1.6 for hard materials and more than 1.6 for soft ones [8]. Thus the grown SALA crystal is soft material.

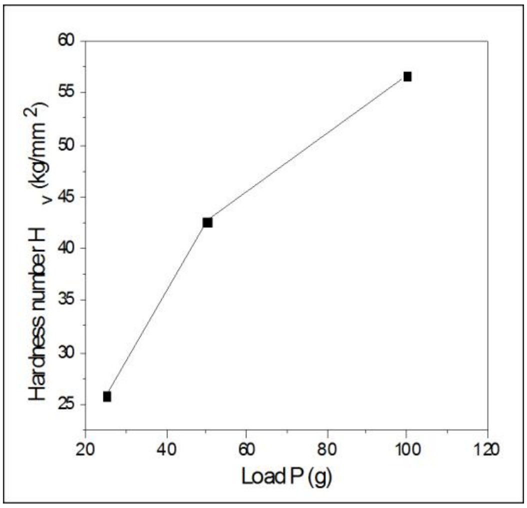

Fig. 2. Plot of hardness number versus load for SALA crystal

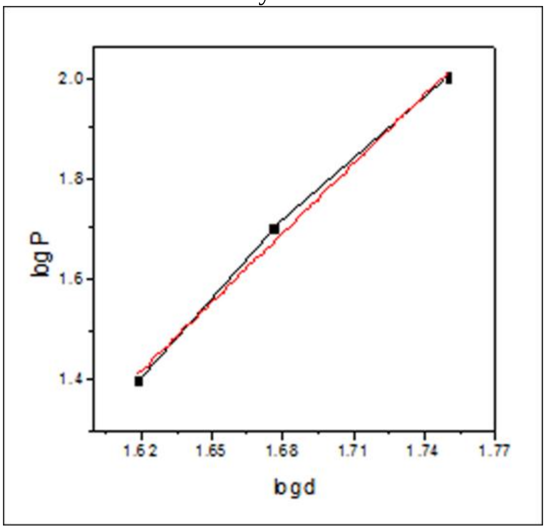

Fig. 3. Plot of log P versus log d for the SALA crystal

The microhardness value correlates with other mechanical properties such as yield strength and stiffness constant. Yield strength [9] is one of the important property for device fabrication is calculated using the following relation for n>2

$$\text{Yield strength } (\sigma_y) = (H_v/3)\,(0.1)^{n-1} \qquad (3)$$

Also, the elastic stiffness constant (C_{11}) has been calculated using Wooster's empirical formula [10]

$$C_{11} = (H_v)^{7/4} \qquad (4)$$

The variation of yield strength and stiffness constant with the different loads for the SALA crystal are shown in the figures 4 and 5. From the graphs, it is clear that the yield strength and stiffness constant increases with increase of load. Hence the SALA crystal has high mechanical strength and strong binding forces between the ions.

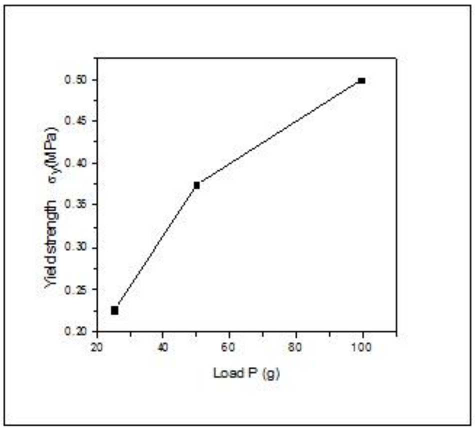

Fig. 4. Variation of yield strength with load for SALA crystal

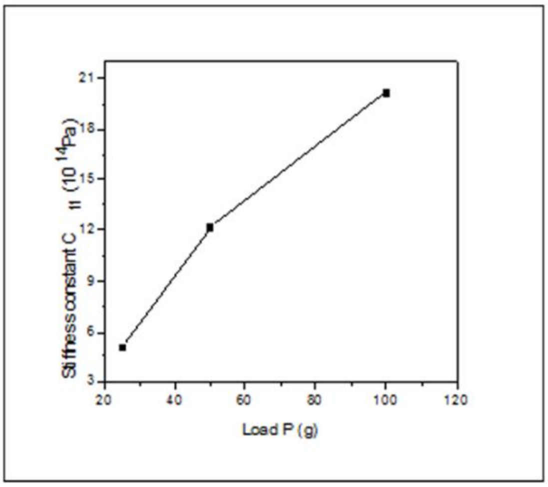

Fig. 5. Variation of stiffness constant with load for SALA crystal

C. UV-vis-NIR Spectral studies

The optical transmission range, transparency cut-off and the absorbance band are the most important optical parameters for laser frequency conversion applications. The UV-vis-NIR transmittance spectrum of transparent, cut and polished crystal of 1 mm thickness SALA crystal was recorded in the wavelength region from 190 to 1100 nm using Perkin Elmer Lambda 35 spectrometer and it is shown in figure 6. The transparency of the grown crystal was about 65 % in the visible region so that SALA crystal can be used for nonlinear optical applications. The UV cut-off wavelength for the grown crystal was found to be242 nm. The optical energy band gap

(E_g) of the material is very closely related to the atomic and electronic band structures.

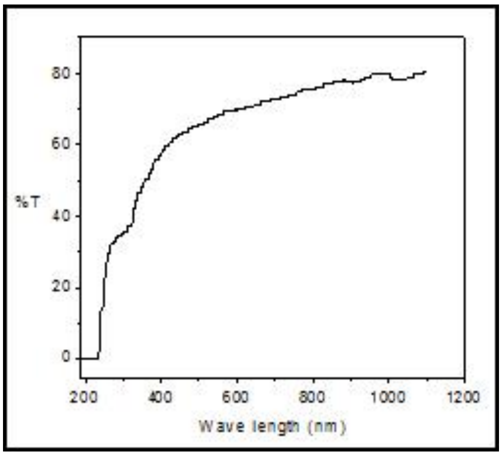

Fig. 6. Optical transmittance spectrumof SALA crystal

The transmittance (T) was used to calculate the absorption coefficient (α) using the formula

$$\alpha = (1/t) \ln (1/T) \qquad (5)$$

where T and t are the transmittance and thickness of the crystal. For the direct band gap, the absorption coefficient (α) obeys the Tauc's relation [11] for photon energy (hν),

$$(\alpha h\nu)^2 = A (h\nu - E_g) \qquad (6)$$

where A is a constant, h is the Planck's constant and ν is the frequency of the incident photons. The optical band gap is obtained by plotting the graph between hν and $(\alpha h\nu)^2$ as shown in figure 7.

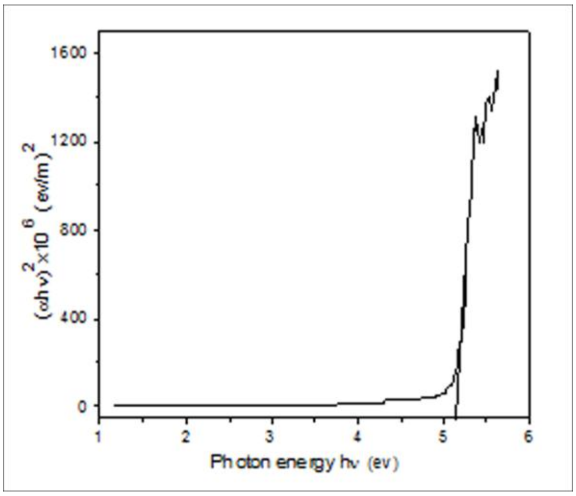

Fig. 7. Tauc's plot for SALA crystal

From the above graph, the optical energy gap of SALA crystal is determined as 5.14 eV. It suggests that the transmittance and the band gap of SALA have increased due to adding of sodium acetate into L-alanine crystal [12].

D. Electrical properties by impedance analysis

Impedance Spectroscopy is a valuable tool for studying electrical properties of the materials. This analysis is basically unambiguous and provides a true picture of electrical behavior of the sample. An impedance analyzer (Model: Versa STAT MC) in the frequency range from 1 to 10^6 Hz and silver paste electrode SALA crystal was used to measure the impedance. Electrical impedance is a material property which has two components namely the resistive and the reactive parts. The electrical response of the material can be analyzed by an equivalent circuit, consisting of a resistor and capacitor with parallel combination. In order to simplify the calculations of impedances, the result obtained for the periodic perturbation of an electrical circuit may be represented using complex notation. Then the complex impedance [13, 14] can be represented as

$$Z^* = Z' + Z'' \quad (7)$$

where Z', Z'' are the real and imaginary parts of the impedance respectively. Figure 8 shows a general impedance plot or Nyquist plot of the SALA crystal at 30^o C and one partial semicircular arc is observed due to the bulk effect (ie, bulk resistance). Bulk resistance is found to be 1.284 $x10^9$ ohm.

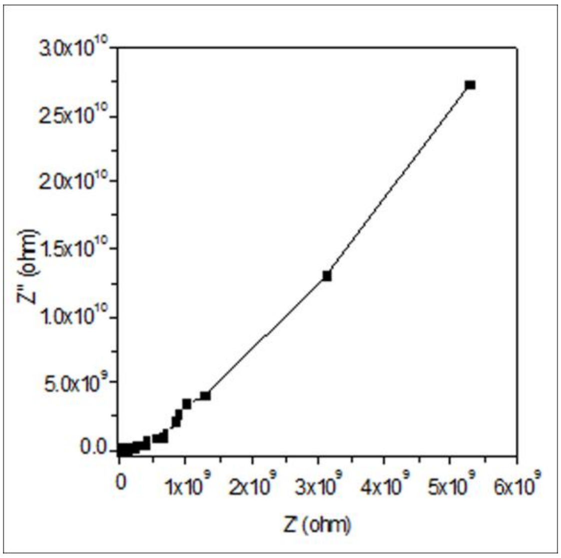

Fig. 8. Nyquist plot of SALA crystal

From the above value, the dc conductivity of the crystal was calculated using the following relation

$$\sigma_{dc} = d/R_bA \quad (8)$$

where A is the area of crystal surface and d is the thickness of the crystal. The dc conductivity was found to be 9.735 $x10^{-8}$

m^{-1} mho at 30^oC. This low value of conductivity suggests that the SALA crystal has low number of defects.

III. CONCLUSION

Optically good quality transparent SALA single crystals have been grown by the slow evaporation method. Single crystal X-ray analysis shows that the orthorhombic system. The mechanical properties were carried out to obtain the hardness parameters of the grown crystals. The transmittance spectrum shows existence of wide transparency window suitable for optoelectronic applications. Using the impedance data the Nyquist plot is drawn and bulk resistance, dc conductivity were calculated for SALA crystal.

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