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RESEARCH ARTICLE

OPTICAL, MECHANICAL AND DIELECTRIC PROPERTIES OF L-ALANINUM SUCCINATE (LAS) SINGLE CRYSTAL

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ABSTRACT

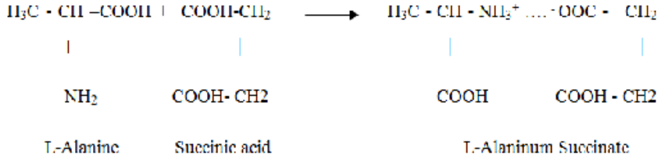
Succinic Acid (SA) and L- Alaninum Succinate (LAS) single crystals have been grown by slow evaporation method. The band gap energies of the SA and LAS crystals have been calculated using cut off frequencies observed in the UV-Vis spectrum. The presences of various functional groups in the crystals were identified by FTIR spectrum. The nonlinear optical property of the grown crystal was confirmed by second harmonic generation technique. Dielectric studies were carried out as a function of frequency for three different temperatures. Hardness studies were performed on LAS crystal and Meyer's index confirmed that the crystal belongs to soft material category.

INTRODUCTION

Ferroelectric materials are used in a wide variety of electronic, mechatronic and non-linear optical devices due to their pronounced dielectric, piezoelectric and pyro electric properties. Ferroelectric succinic acid (SA) exhibits good pyroelectric properties (Krishnan *et al*., 2007) Succinic acid has been used in many biological and industrial applications (Zeikus *et al*., 1999; Jain *et al*., 1989; Hong *et al*., 2000). Succinic acid has been used as a matrix in infrared (IR) MALDI analytical methods (Talrose 1999; *Budnik et al., 2000;* Feldhaus *et al*., 2000; Hagberg 2003; Carnahan *et al*., 2002; Remenar *et al*., 2003). In the present work, we have reported the growth of organic SA and LAS crystals and the results obtained by UV-Vis spectroscopy, Fourier transform infrared transmission spectrum, Vickers Hardness, Dielectric and NLO studies

MATERIALS AND METHODS

The nonlinear optical SA and LAS crystals have been grown by slow evaporation solution method. Among the various methods of growing single crystal, the method of solution growth at low temperature occupies a prominent place owing to its versatility and simplicity. During growth procedure water was used as the solvent due to its relatively high solubility Analytical grade succinic acid dissolved in double distilled water was stirred continuously for an hour to get the saturated solution. To remove impurities such as solid and dust particles, the saturated solution was filtered using filter paper. Then the filtered solution was covered by polythene paper in which holes were made for slow evaporation. Crystallization was allowed to take place by slow evaporation at a temperature range of 35º C in a constant temperature bath of accuracy ± 0.01º C. After a period of 20 days, colourless and transparent SA single crystal of size 1.6cm x 0.8cm x 0.3cm was harvested. The LAS crystal was synthesized from commercially available L-Alanine (AR grade) and succinic acid (AR grade) taken in equimolar ratio. The calculated amount of reactants were thoroughly dissolved in double distilled water and stirred continuously for 6 hours using magnetic stirrer to obtain homogeneous solution. Then the solution was slowly evaporated until the solvent was completely dried. The purity of the synthesized salt was further increased by successive recystallization process. Colourless and transparent LAS single crystal of size 1.5cm x 1cm x 0.4 cm was grown within a period of three weeks. In order to study the influence of pH on the growth rate, crystals have been grown with the solution of pH values 3, 5 and from solution of pH5 good quality crystals were obtained. The LAS crystal was synthesized from L-Alanine and Succinic acid as represented by the following reaction:



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RESULTS AND DISCUSSION

Transmittance studies

Good optical quality and well defined electronic structured single crystals have been mainly used for many technologically important device applications. The UV-Vis transmittance of SA and LAS crystals were recorded using shimadzu-160 spectrometer. The spectrum recorded in the wavelength range 200–800 nm is shown in Fig. 1(a) & 1(b) respectively. From the transmittance spectra, it is observed that SA and LAS crystals have high transmittance in the UV and entire visible region. The absorption in the near UV region in the crystal represents the delocalized electron available for charge transfer (Ushasree *et al.*, 1999). The UV cut-off wavelength for SA and LAS crystals is found to be at 224 nm and 218 nm respectively. The wide range of transparency (90% for SA and 95% for LAS) suggests that both grown crystals can be utilized in the field of optoelectronic devices (Bairava Ganesh *et al.*, 2007)

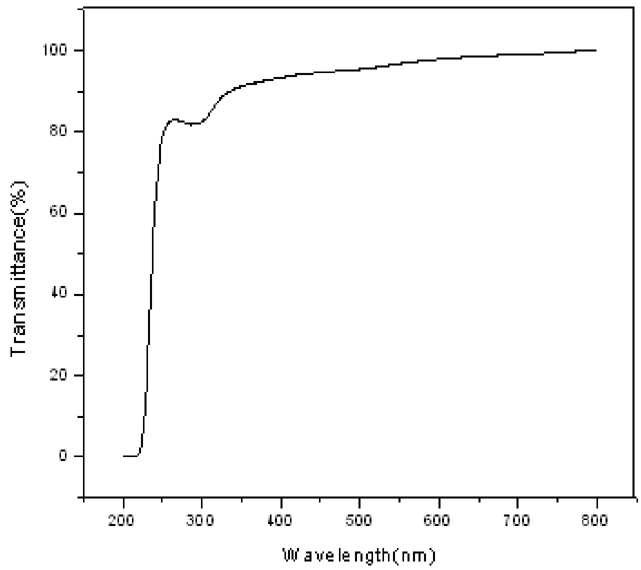

Fig.1 (a). UV-Vis transmission spectra of SA crystal

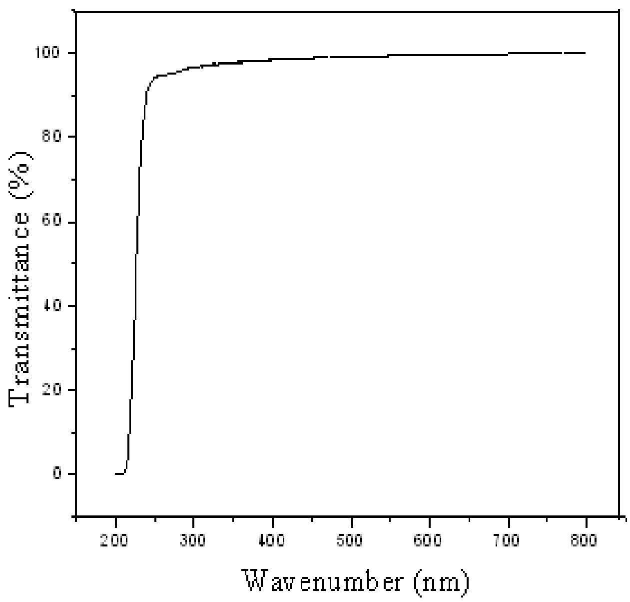

Fig.1 (b). UV-Vis transmission spectra of LAS crystal

Optical band gap

The dependence of optical absorption coefficient on the photon energy aids in study of band structure and the type of transition of electrons in materials (Tauc *et al.*, 1966). The optical absorption coefficient (α) was calculated from the transmittance spectra using the following relation

$$\alpha = \frac{2.3036 \log (1/T)}{d}$$

The optical band gap, E_g = 3.46eV and 5.71 eV respectively for SA and LAS single crystal have been obtained by extrapolating the linear portion of the plots of (αhν) vs (hν) as shown in Fig. 2 (a) & 2(b). As a consequence of wide band gap, the grown crystal exhibits large transmittance in the entire visible region (Justin Raj *et al.*, 2008).

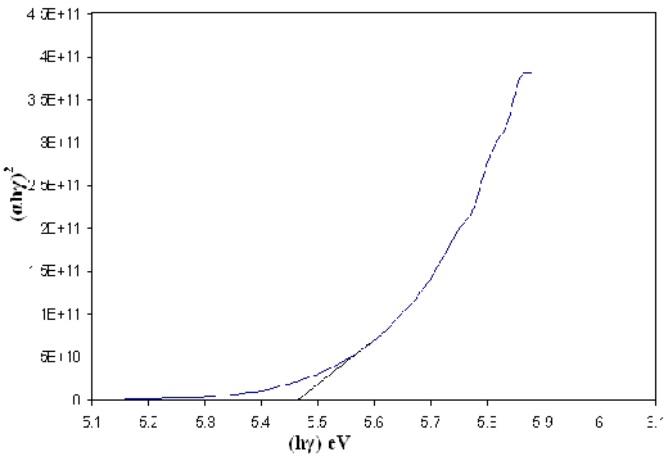

Fig.2 (a). α vs photon energy of SA single crystal

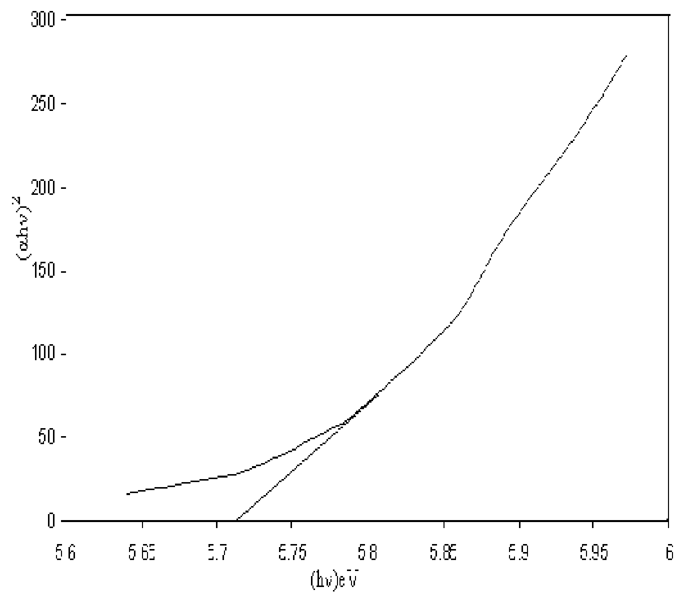

Fig. 2(b). α vs photon energy of LAS single crystal

FTIR analysis

Fourier transform infrared spectrum was recorded by using Shimadzu FT-IR 8400 spectrophotometer in the region 400-

4000cm^{-1}. FTIR spectrum of SA and LAS crystals are shown in Fig.3 (a) & 3 (b) respectively. The observed vibrational frequencies and their assignment are listed in Table.1. The presence of NH_3^+ group in LAS is identified at 3082 cm^{-1} which may be due to protonation of NH_2 group by the COOH group of succinic acid (Sajan *et al*., 2004). The peak in the region 1612 cm^{-1} appears due to NH_3^+ bending vibrations. The strong absorption at 1411 cm^{-1} indicates the symmetric stretching vibration frequency of carbonyl group for LAS crystal. The peak position of 910 cm^{-1} for SA crystal got shifted to higher wave number of 918 cm^{-1} for LAS crystal. This upward shift can be attributed to the interaction of O-H group of succinic acid with COO^- group of amino acids. The bending and rocking vibrations of COO are observed at 771 cm^{-1},648 cm^{-1} and 540 cm^{-1} for LAS crystal and at 636 cm^{-1},443 cm^{-1} for SA crystal (Krishnan *et al*., 2008). CH_2 wagging (1303cm^{-1}) and CH_3 bending (1454 cm^{-1}) vibrations are also observed in LAS crystal (Ramachandra Raja *et al*., 2009).

Table 1. FTIR frequency assignment for SA and LAS

SA Wavenumber (cm^{-1})	Assignment	LAS Wavenumber (cm^{-1})	Assignment
2646	O H stretching	3082	NH_3^+ asymmetric stretching
1689	C=O stretching	1612	NH_3^+ bending
1303, 1199	C-O stretching	1454	CH_3 bending
910	O-H out of plane	1411	COO^- symmetric stretching
636	COO^- bending	1361	CH_3 symmetric bending
443, 543	COO^- rocking	1303	CH_2 Wagging
		1149	NH_3^+ wagging
		1111	NH_3^+ rocking
		1014	CH_3 rocking
		918	CCN symmetric stretching
		848	C-CH_3 bending
		771,648	COO^- bending
		540	COO rocking

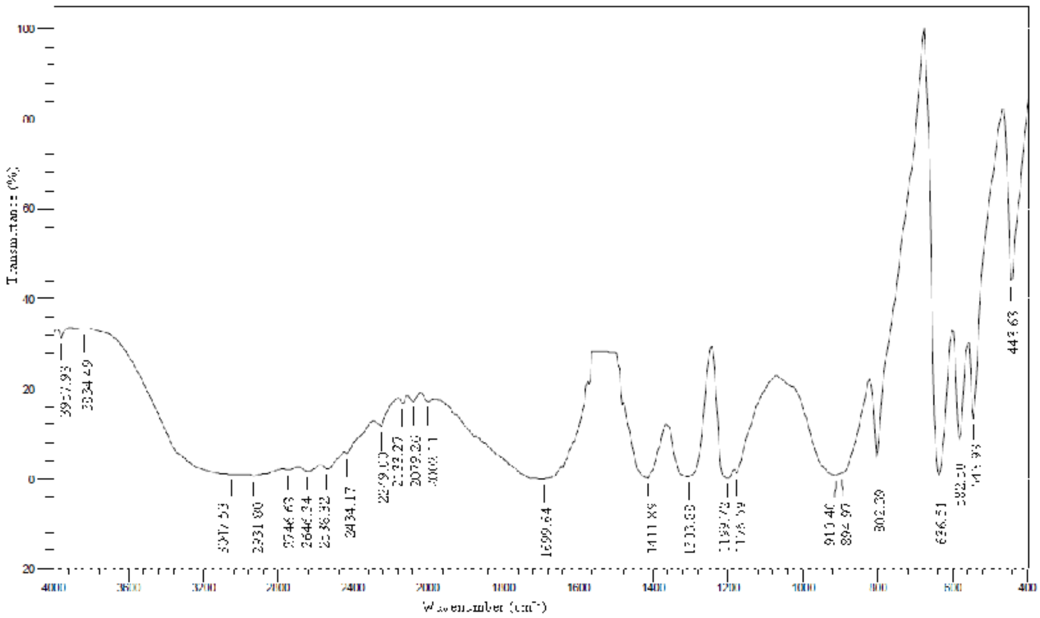

Fig. 3(a). FTIR spectra of SA crystal

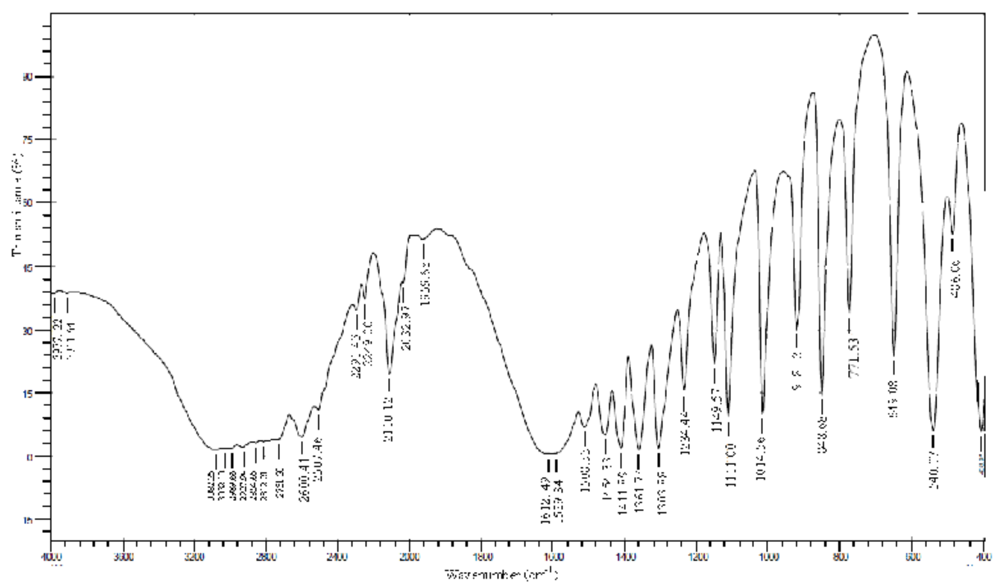

Fig. 3(b). FTIR spectra of LSA crystal

Mechanical analysis

Vickers micro-hardness studies have been carried out using the instrument HMV 2T- SHIMADZU. The indentation hardness values have been measured as the ratio of applied load to the surface area of indentation. Indentations were carried out using indenter for three different loads. Vickers micro - hardness number was computed by using Hv = 1.8544 P/d^2, where P is the load applied, d is the diagonal length of impression (Mott, 1956). Fig. 4(a) shows the plot of hardness number with load indicating the reverse indentation size effect (ISE) where the hardness value increases with increasing load. The indented surface of the sample had multiple cracks around indentations when load P exceeds 100g and this may be due to the release of internal stress generated locally. The value of 'n' has been estimated as 3.13 from the slope of log P vs. log d plot which is shown in the Fig.4 (b). Onitsch and Hanneman (Onitsch, 1947) have shown that the value of n comes out to be 1–1.6 for hard materials and more than 1.6 for soft materials. Thus LAS crystal belongs to soft material category as value of 'n' is 3.13.

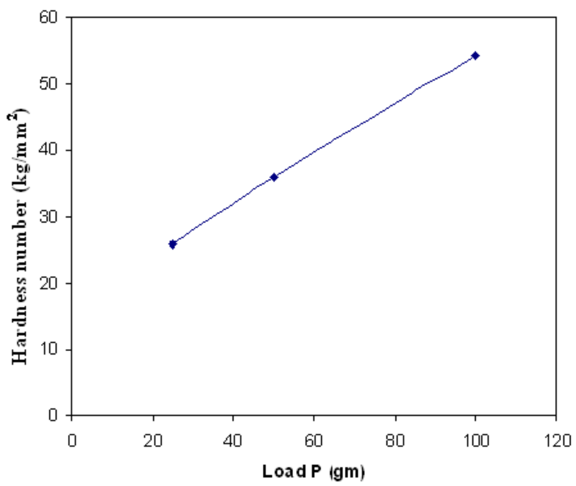

Fig. 4(a). Variation of hardness number with load for LAS crystal

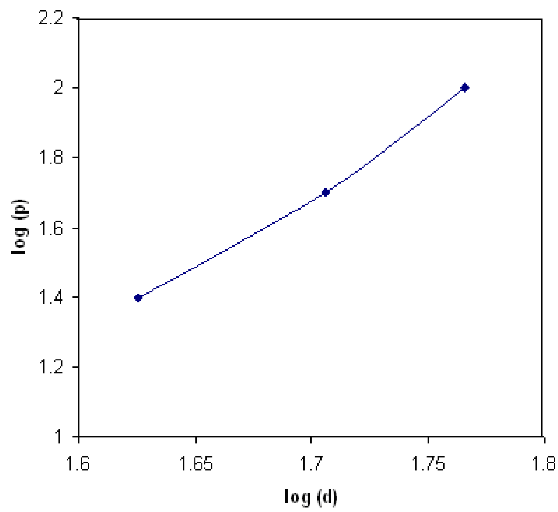

Fig. 4(b). log (P) Vs log (d) for LAS crystal

Dielectric studies

The dielectric characteristics of the material help to know the transport phenomena and the lattice dynamics in the crystal. It also gives information about the nature of atoms, ions, bonding and their polarization mechanism in the material. Dielectric study was carried out using LCR meter for LAS single crystal. The dielectric constant have been calculated using the relation,

$\varepsilon' = Cd / \varepsilon_0 A$

where d is the thickness and A is the area of the sample. The response of dielectric constant as a function of frequency is shown in Fig.5 and found that the dielectric constant decreases with increasing frequency and attain saturation at higher frequencies. Dielectric studies furnish great deal of information regarding the dielectric constant that arises from the contribution of different polarizations, namely electronic, ionic, atomic, space charge, etc., developed in the material subjected to the electric field variations. The large dielectric constant at low frequency for the crystal in the present study is due to space charge polarization arising at the grain boundary interfaces. The low value of dielectric constant at higher frequency reveal the good optical quality of the grown crystal with less defect, which becomes the desirable property for the material to be used in various optical and communication devices (Balarew and Duhlew, 1984).

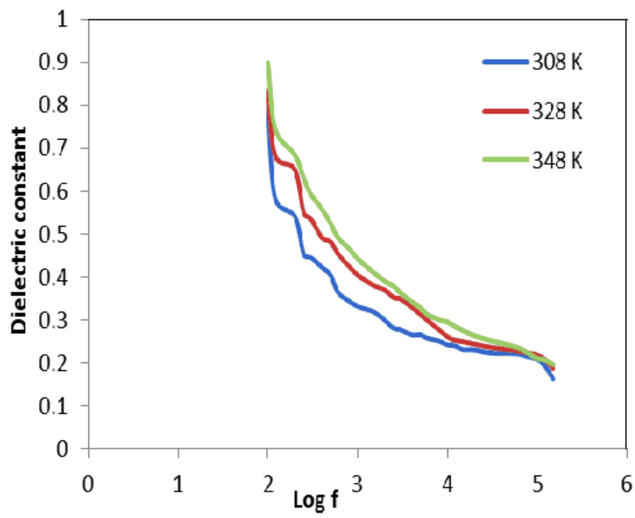

Fig. 5. Dielectric constant for LAS single crystal

Second harmonic generation analysis

The second harmonic generation (SHG) efficiency of the grown crystal has been measured using the technique developed by Kurtz Powder technique (Kurtz and Perry, 1968). An Nd: YAG laser producing pluses with a width of 8 ns and repetition rate of 10 Hz was used. SHG efficiency was observed as 44 % of that of the standard KDP (Natarajan *et al*., 2008).

Conculsion

Good optical quality SA and LAS single crystals have been grown by slow evaporation technique. The optical studies confirms the high transparancy of the crystal and its suitabality for optical device fabrication. The presence of fuctional groups and production of NH_3^+ ion are studied by FTIR spectrum . Vickers's micro hardness test shows that the LAS crystal belong to the category of soft material. The SHG analysis and very low dielectric constant value proves that the LAS crystals are potential nonlinear optical materials.

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