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Studies on Growth and Chracterization of Undoped and L-Alanine Doped Sodium Sulfate Semi Organic Crystal

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Abstract: ***Semi organic non-linear optical crystal of undoped and L-alanine doped sodium sulfate have been synthesized and grown successfully from aqueous solution by slow evaporation method. The grown crystal was characterized by different instrumentation techniques such as FTIR, UV-Vis, Dielectric, Hardness test. The grown crystal was subjected to FTIR studies that reveals the functional groups and the optical characters were analyzed by UV-Vis spectral studies. Vickers Hardness studies were performed in order to evaluate the mechanical strength of the grown crystals. The dielectric studies proved that the crystals possessed a low dielectric constant values at higher frequencies, this suggests an enhanced optical quality with less defects.***

Keywords: Slow evaporation, FT-IR, Dielectric, Vickers hardness, UV-Vis spectral, Amino acid

1. Introduction

Crystals are the unacknowledged pillars of modern technology. Without crystals, there would be no electronic industry, no photonic industry, no fiber optic communications, which depend on materials/crystals such as semiconductors, superconductors, polarizers, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, non-linear optics, piezo-electric, electro-optic, acousto-optic, photosensitive, refractory of different grades, crystalline films for microelectronics and computer industries. Crystal growth is an interdisciplinary subject covering physics, chemistry, material science, chemical engineering, metallurgy, crystallography, mineralogy, etc. In the past few decades, there has been a growing interest on crystal growth processes, particularly in view of the increasing demand of materials for technological applications [1]. Hence, growth of single crystals has become inevitable for further research and technology. The search of new materials is primarily focused on increasing the nonlinearity. With progress in crystal growth technology, materials having attractive nonlinear optical properties are being discovered. This has enabled the commercial development of single crystals with promising nonlinear optical properties. Large size crystals are essential for device fabrication and efforts are taken to grow large crystals in short durations by fast growth techniques. The present day demand is for large and high quality NLO, Ferro-electric and piezo-electric single crystals with minimum defects [2].The organic crystals have been very large nonlinear susceptibilities than the inorganic one, but it has low laser damage threshold, inadequate transparency, poor optical quality, lack of robustness, inability to produce large crystals. In the case of inorganic NLO materials, though they have excellent mechanical and thermal properties, they have relatively modest optical linearity's due to the lack of extended π-electrons delocalization [3, 4]. Hence in the several years research is focused on new types of NLO materials which combine the advantages of organic and inorganic materials called semi organic materials [5-10]. Another interesting class of semi organic crystals, which receive wider attention in the recent past includes, the analogs of L-arginine, L-histidine, L-alanine, L-proline, L-phenylalanine etc.The present work reports the growth and characterization of undoped and L-alanine doped sodium sulfate, new semi organic crystal which have high optical quality [11].

2. Experimental Procedure

Synthesis and Crystal growth

The undoped and L-alanine doped sodium sulfate crystals has been grown from aqueous solution by slow evaporation method. The crystal was synthesized by dissolving sodium sulfate in distilled water. This was stirred for 2 hours at room temperature (32^0c). The solution was purified by repeated filtration. The saturated solution was kept in a beaker covered with filter paper and the solution was left undisturbed. As a result of slow evaporation, after 4 to 5 weeks white and pure crystals were obtained. The same procedure was followed to grow L-alanine mixed sodium sulfate crystals.

3. Characterization Techniques

3.1 FTIR spectrum analysis

The FTIR spectroscopy studies were used to analyze the presence of functional groups in synthesized compound. The FTIR spectra of pure sodium sulfate and L-alanine doped were recorded using KBr pellet technique employing Barker, IFS 66 FTIR spectrometer in the range 4000-400 cm^{-1} and are shown in Fig 1(a) and (b). The characteristic vibrational frequencies of the functional groups of pure and L-alanine have been compared. A close observation of FTIR spectra of pure and amino acid doped specimens reveal that doping generally results in small shifts in some of the characteristic vibrational frequencies. It could be due to lattice strain as a result of metal doping. The observed band along with their vibrational assignments have been tabulated in the table 1(a) and (b).

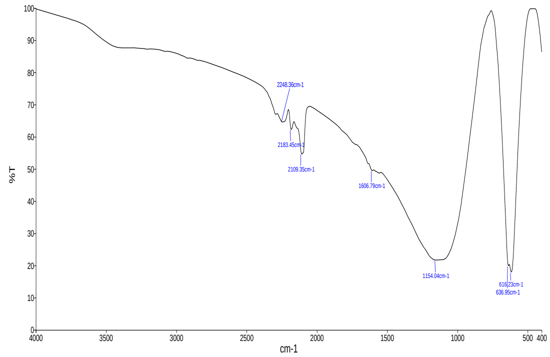

Figure 1(a): FTIR spectrum of undoped sodium sulfate crystal

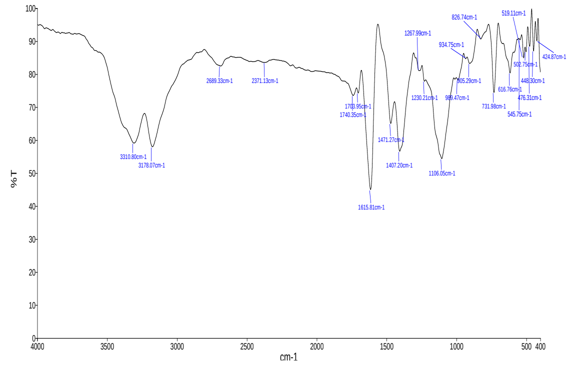

Figure 1(b): FTIR spectrum of L-alanine doped sodium sulfate crystal

Table 1(a): FTIR data of undoped sodium sulfate crystal

Wavelength cm^{-1}	*Functional groups*
2248.36	Alkyne stretching
1606.79	Amine bending
1154.04	Alkyl halide stretching
1407.20	Sulfate stretching

Table 1(b): FTIR data of L-alanine doped sodium sulfate crystal

Wavelength cm^{-1}	*Functional groups*
3310.80	Amine stretching
2689.33	Carboxylic acid stretching
1740.35	Aldehyde stretching
1625.81	Unsaturated ketone stretching
1407.20	Sulfate stretching
1267.99	Alkyl aryl ether stretching
989.47	Alkene bending

3.2 UV-Visible spectrum analysis

The optical transparencies of the grown crystals were analyzed by taking the UV-Visible spectra using LAMBDA-35 spectrometer wavelength range between 200 nm to 1200 nm. The observed spectra of undoped and L-alanine doped sodium sulfate crystals are shown in Fig 2(a) and (b). The lower cutoff wavelength of these crystals were found to be about 219nm and 238nm. The percentage of transmission for sodium sulfate is about 79% and L-alanine doped is 98%, the transmission window range was obtained as 219nm to 1100nm and 238nm to 1100nm. The resultant spectrum shows that the crystals has very high absorption in entire visible and IR region. Hence these crystals can be used for optoelectronic applications and in the second harmonic generation from the Nd: YAG lasers.

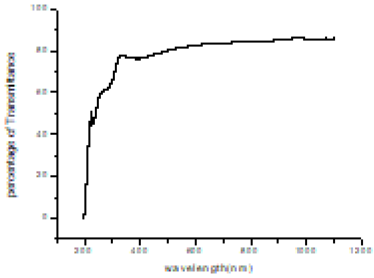

Figure 2(a): UV-Visible spectrum of undoped sodium sulfate

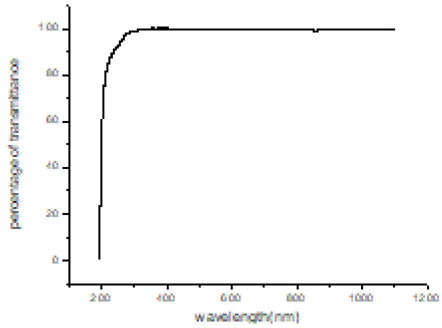

Figure 2(b): UV-Visible spectrum of L-alanine doped sodium sulfate

Optical energy band gap

The dependence of optical absorption coefficient with the photon energy helps to study the band structure and the type of transition of electron. The absorption coefficient (α) were determined using Beer's law

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

Where T is the transmission and d is the thickness of the cell. As the indirect bandgap, the crystal under study has an absorption coefficient (α) obeying the following relation for high photon energies

$$\alpha = \frac{A(h\nu - E_g)^2}{h\nu} \quad (2)$$

Where Eg is optical bandgap of the crystal and A is a constant. The plot of variation of Photon energy (E) in eV and $(\alpha h\nu)^2$ is shown in Fig 3 (a) and (b).

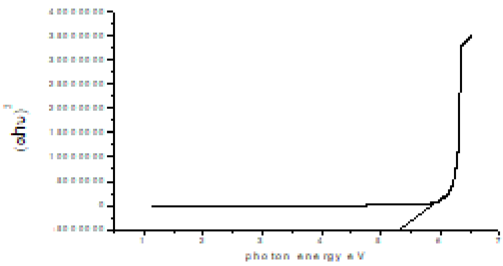

Figure 3(a): Bandgap curve for undoped sodium sulfate

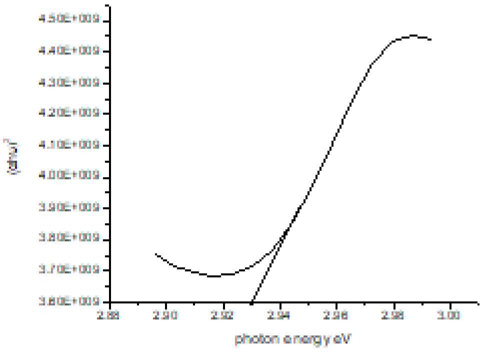

Figure 3(b): Bandgap curve for L-alanine doped sodium sulfate

From the graph the band gap for undoped sodium sulfate and L-alanine doped sodium sulfate crystals was found to be 5.28eV and 2.93 eV.

3.3Dielectric studies

Dielectric measurements on undoped sodium sulfate and amino acid doped sodium sulfate single crystals were carried out using a HIOKI 3532-50 LCR meter as a function of frequency (50 Hz – 20 MHz) and temperature (32°c). From the dielectric measurement, the capacitance of parallel plate capacitor as a function of frequency and temperature was measured. The dielectric constant ε^r and loss factor ε` were calculated using the following relations.

$$\varepsilon^r = Cd/\varepsilon^0 A \qquad (3)$$

$$\varepsilon = \varepsilon^r tan\delta \qquad (4)$$

Here C is the capacitance of the parallel plate capacitor (pF), d is the thickness of the crystal. A is the area of the crystal acting as the dielectric, ε_0 is the permittivity of free space $(8.854 \times 10^{-12} F/m)$ and tanδ is the dissipation factor. Plots of ε^r and ε` against log (frequency) at room temperature is shown in Fig 4 and 5.

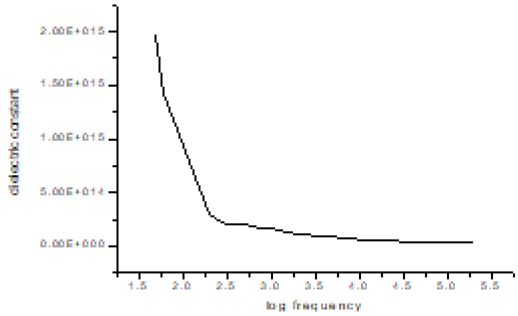

Figure 4(a): Dielectric constant profile of undoped crystal

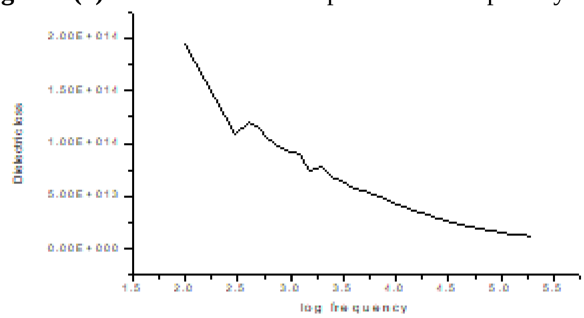

Figure 4(b): Dielectric loss profile of undoped crystal

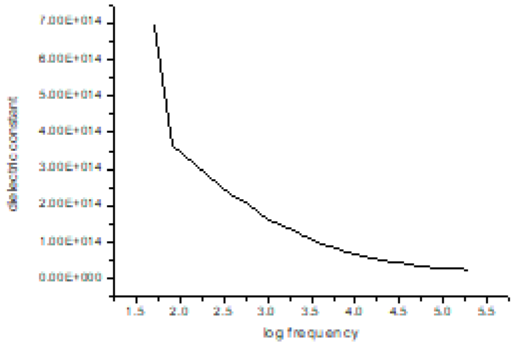

Figure 5(a): Dielectric constant profile of doped crystal

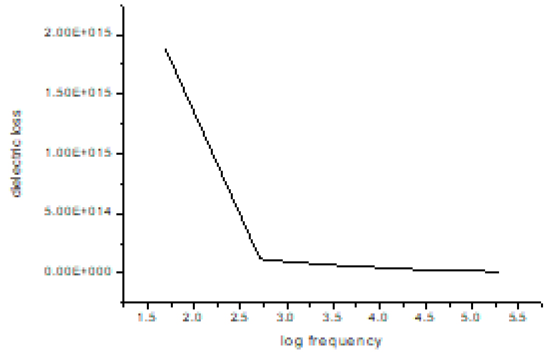

Figure 5(b): Dielectric loss profile of doped crystal

From the dielectric constant profiles, it is evident that the dielectric constant decreases with increasing frequency and increases with increasing temperature.The increase in dielectric constant at low frequencies is attributed to the dependence of electronic, ionic, orientational and space charge polarization and the increase in dielectric constant with temperature leads to the conclusion that the thermal excitations of atoms about their lattice points results in disordering the lattice. Here the space charge contribution to polarization is due to the purity of the material. Dielectric constant at low frequencies are comparable to optical frequencies, which lead to minimization of the phase mismatch between optical and electrical pulses in high-speed travelling wave devices. In accordance with the Miller rule, the lower value of dielectric constant at high frequencies is a suitable parameter for the enhancement of SHG coefficient.

3.4 Mechanical studies: Vicker's Hardness test

The Vicker's micro hardness number Hv of the crystal was calculated using the relation

$$H_v = \frac{1.8544\,p}{d2}\ kg/mm^2$$

The graph was plotted between load V_s Hardness number is shown in Fig 6 (a) and (b). The Vicker's hardness number increases for increasing loads. Work hardening coefficient 'n' were also calculated by using Mayers' relation by plotting a graph between log p versus log d, which is shown in Fig 7 (a) and (b). The data are given in table 2 (a) and (b).

Table 2(a): Hardness data for undoped sodium sulfatecrystal

Load P in grams	*HV (kg/mm²)*	*Log d*	*Log p*
25	28.9	-4.39808	-1.60206
50	45.9	-4.34739	-1.30103
100	65.15	-4.27306	-1

Table 2(b): Hardness data for L-alanine doped sodium sulfate crystal

Load P in grams	*HV (kg/mm²)*	*Log d*	*Log p*
25	34.2	-4.43427	-1.60206
50	35.25	-4.2902	-1.30103
100	39.85	-4.16614	-1

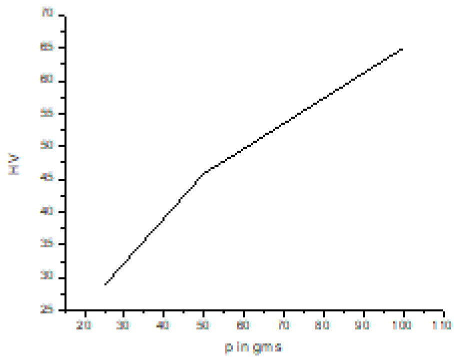

Figure 6(a): Plot of applied load Vs hardness number for sodium sulfate

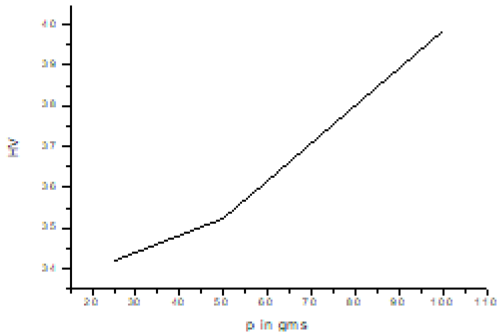

Figure 6(b): Plot of applied load Vs hardness number for L-alanine doped sodium sulfate

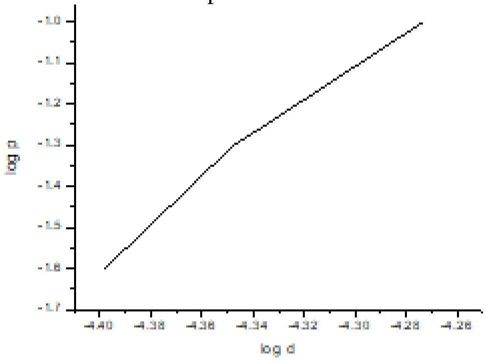

Figure 7(a): Graph between log d and log p of sodium sulfate

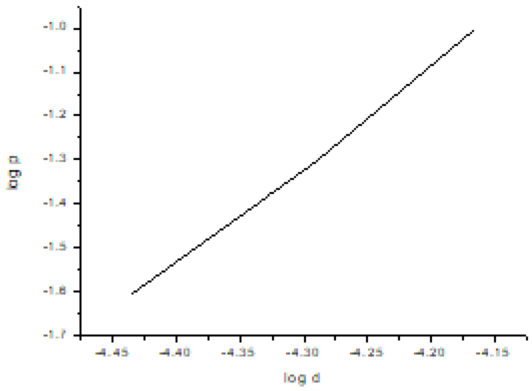

Figure 7(b): Graph between log d and log p of L-alanine doped sodium sulfate

From Meyer`s law $p = ad^n$

Connecting the applied load (p) and diagonal length (d)of the indentation, the work hardening coefficient ‘n’ is calculated. The calculated value of ‘n’ for sodium sulfate and L-alanine doped sodium sulfate is 4.75 and 2.2. Here ‘a’ is constant for a given material.

The work hardening coefficient ‘n’ is found for sodium sulfate and L-alanine doped crystals by taking slope in the straight line of the graph drawn between log p and log d. which is shown in fig 7 (a) and (b).

From Onitsch [12] and Hanneman [13], ‘n’ lies between 1 and 1.6 for hard materials and is greater than 1.6 for soft materials [14, 15]. From the calculated values of ‘n’, it is suggested that the grown crystals are soft materials.

4. Conclusion

The potential semiorganic NLO crystals of pure and amino acid doped sodium sulfate were grown by slow evaporation method. The grown crystals were subjected to characterization techniques in order to assess the spectral, optical, mechanical and dielectric properties. The functional groups present in the crystals was determined by using FT-IR analysis and were tabulated which confirms the compounds. UV-Vis analysis was used for the determination of the optical quality of the crystals. The optical behaviors are analyzed using UV-Vis Spectrometer. It reveals that the crystals have an extended transparency down to UV and the bandgap estimated for the pure & amino acid doped sodium sulfate crystals. From the optical response curve, the bandgap energy was found. By tailoring the absorption coefficient and tuning the band gap of material we can achieve the desired material suitable for fabricating various layers of optoelectronic devices. Vickers Hardness studies were performed in order to evaluate the mechanical strength of the grown crystals. The dielectric studies proved that the crystals possessed a low dielectric constant values at higher frequencies, this suggests an enhanced optical quality with less defects.Owing to all these properties undoped and amino acid doped sodium sulfate could be a promising material for NLO applications.

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