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Growth, Optical, Hardness and Dielectric Studies of L-alanine Crystals Doped with Sodium Nitrate

KEYWORDS
amino acid; L-alanine; doping; crystal growth; NLO; microhardness; XRD; band gap

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ABSTRACT *L-alanine is a conditionally essential amino acid and it is an important source of energy for muscle tissue, the brain and central nervous system. L-alanine is a nonlinear optical (NLO) material and a source of second harmonic generation. In this work, the properties of L-alanine crystal have been improved by adding sodium nitrate as the dopant. The single crystals of pure and sodium nitrate doped L-alanine were grown by slow evaporation method and the grown crystals were characterized by studies like XRD studies, SHG studies, mechanical studies, optical studies and dielectric studies and the obtained results are discussed.*

Introduction

In the past decade, the crystals of the amino acids and their complexes have been subjected to many investigations by several researchers and a series of amino acids such as glycine, L-arginine, L-histidine, L-threonine etc have been considered for NLO and other applications [1-4]. L-alanine is one of the simplest amino acid often used as a model for the investigation of various types of intermolecular and intramolecular interactions, which are expected to be present in relatively complex and biologically relevant molecules. Moreover, it is an ideal candidate for a wide range of applications in electron paramagnetic resonance (EPR) dosimetry due to the particular properties of the associated radiation-induced radicals such as the linear signal response over a wide dose range, good dose yield factors, tissue equivalence and stability of the EPR signal [5-7]. L-alanine is an NLO material and its properties can be improved by adding a dopant like sodium nitrate. This work aims to prepare and characterize single crystals of undoped and sodium nitrate doped L-alanine.

Crystal growth

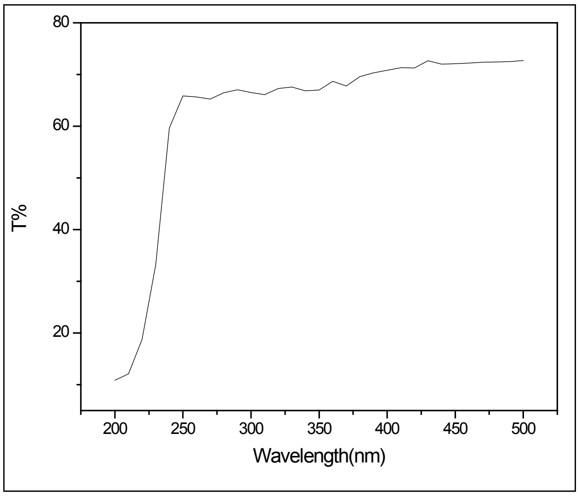
Pure chemicals of L-alanine and sodium nitrate were purchased commercially. The saturated solution of L-alanine was prepared using double distilled water as the solvent. The solution was stirred well using a magnetic stirrer for 1 h and it was filtered. The filtered solution was kept in a perforated covered beaker for slow evaporation. It took 25 days to grow pure L-alanine crystals. To grow sodium nitrate doped L-alanine crystals, 5 mole % of sodium nitrate was added into the solution of L-alanine and the doped crystals were grown by slow evaporation.

Single crystal X-ray diffraction (XRD) studies

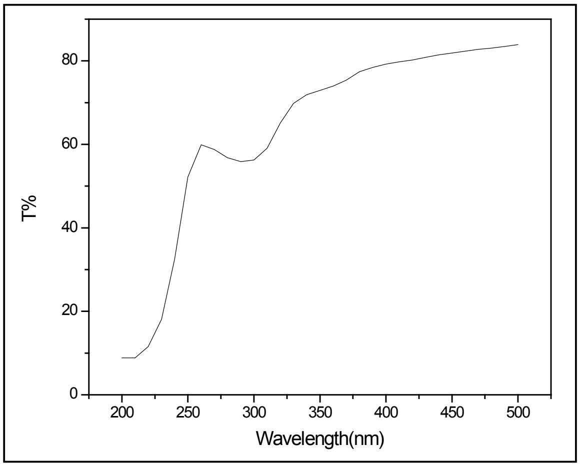
The grown crystals of undoped and sodium nitrate doped L-alanine were subjected to single crystal XRD studies using a Bruker-Nonious MACH3/CAD4 single crystal X-ray diffractometer and XRD data were obtained. The obtained data are a = 5.723(1) Å, b = 6.022(3) Å, c=12.347(3) Å, $\alpha = \beta = \gamma = 90°$ and a = 5.734(2) Å, b = 6.028 (4) Å, c=12.354(2) Å, $\alpha = \beta = \gamma = 90°$ for pure and sodium nitrate doped L-alanine crystals respectively. From the data, it is observed that the structure is orthorhombic. The structure is not changed when L-alanine crystal is doped with sodium nitrate. The obtained data for pure L-alanine crystal in this work are found to be the same as reported in the literature [8].

Linear optical studies

UV-visible transmittance spectra for pure and sodium nitrate doped L-alanine crystals were recorded using a A Varian Cary 5E UV-visible-NIR spectrophotometer in the wavelength range 200 – 1100 nm. A crystal thickness of about 1.5 mm was used for these studies. UV-visible-NIR transmittance spectra of pure and sodium nitrate-doped L-alanine crystals in the wavelength range 200-500 nm are shown in figure 1. This spectral study may be assisted in understanding electronic structure of the optical band gap of the crystal. The study of the absorption edge is essential in connection with the theory of electronic structure, which leads to the prediction of whether the band structure is affected near the band extreme. From the transmittance spectra, it is noticed that pure and sodium nitrate doped L-alanine crystals have high transmittance in the entire visible-NIR region of the spectra and this property enables the materials for optoelectronic applications and second harmonic generations from Nd:YAG laser. For both the samples, the cut-off wavelength is observed to be at 237 nm. It is observed that doping L-alanine crystal with sodium nitrate increases the percentage of transmission and does not alter the lower cut-off wavelength. Absorption in the near ultraviolet region arises from electronic transitions associated within the samples. Using the formula $E_g = 1240 / \lambda$ (nm), the band gap is calculated to be 5.23 eV. From the results it is noticed that there is considerable absorption around 300 nm in the spectrum of sodium nitrate doped L-alanine crystal and it indicates that the dopant has entered into the host L-alanine crystal.



(a)



(b)

Fig.1: UV-visible transmittance spectra for (a) pure and (b) sodium nitrate doped L-alanine crystals

Mechanical properties

Mechanical property of the samples was studied by measuring microhardness number with various applied loads. Here low loads are applied to measure the hardness of the samples. Microhardness analysis was carried out using Leitz Weitzler hardness tester fitted with a diamond indenter. A well polished crystal was placed on the platform on the Vickers microhardness tester and the loads of different magnitude were applied over a fixed interval of time of 10 s. Figure 2 shows the variation of hardness number with different loads for pure and sodium nitrate doped L-alanine samples and it is noticed that Vickers hardness number(H_v) increases with the applied load satisfying the reverse indentation size effect. From the results, it is observed that the hardness of L-alanine crystal increases when it is doped with sodium nitrate. This increase in the hardness value can be attributed to the incorporation of impurity in the lattice of L-alanine crystal. The yield strength is defined as the stress at which a predetermined amount of permanent deformation occurs and it is determined using the formula $\sigma_y = (H_v/3)$ where σ_y is the yield strength and H_v is the hardness of the material. The stiffness constant (C_{11}) for different loads was calculated [9] using Wooster's empirical formula $C_{11} = H_v^{7/4}$ and the calculated values of yield strength and stiffness constant for pure and sodium nitrate doped L-alanine crystals are provided in the table 1. It is observed that yield strength increases with increase of load and hence the grown crystals have relatively high mechanical strength and also it is noticed that the stiffness constant increases with increase of load. High values of C_{11} indicate that the binding forces between the ions are quite strong in the grown crystals.

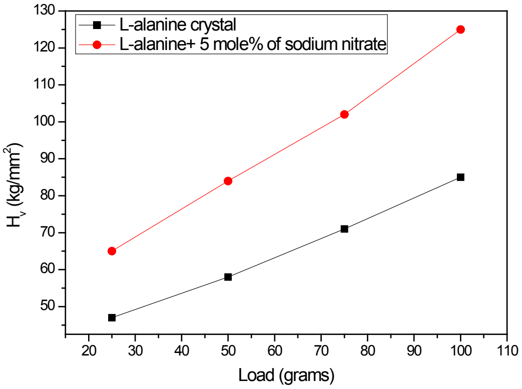


Fig.2: Variation of microhardness number (H_v) with load for pure and sodium nitrate doped L-alanine crystals

Table 1: Values of yield strength and stiffness constant for pure and sodium nitrate doped L-alanine crystals

Sample	Load (grams)	Yield strength (Mega pascal)	Stiffness constant (x 10^{15}) pascal
Pure L-alanine crystal	25	153.53	1.448
	50	189.47	2.092
	75	231.93	2.981
	100	277.67	4.084
Sodium nitrate doped L-alanine	25	212.33	2.554
	50	274.4	4.001
	75	333.2	5.619
	100	408.33	8.021

Second harmonic generation (SHG) studies

Second Harmonic Generation (SHG) is a second-order nonlinear optical (NLO) property and it was tested for the grown pure and sodium nitrate doped L-alanine crystals using the powder technique of Kurtz and Perry [10] using a pulsed Nd:YAG laser(Model: YG501C, λ=1064 nm). The grown crystals were ground to powder of grain size 200-300 μm and the input laser beam was passed through IR reflector and directed on the powdered sample. Potassium Dihydrogen Phosphate (KDP) was used as the reference sample. The SHG behavior was confirmed by the emission of green light (λ = 532 nm) from the samples. The second harmonic generation signal of 9.24 mJ for sodium nitrate doped L-alanine crystal was obtained for an input energy of 0.68 J. But the standard KDP sample gave an SHG signal of 8.8 mJ for the same input energy. Hence, relative SHG efficiency of the doped L-alanine crystal is 1.05 times that of the standard KDP sample. The undoped L-alanine crystal was also subjected to SHG measurement and it is found that the SHG efficiency for L-alanine sample is about 0.35 times that of KDP sample. Hence, the sodium nitrate doped L-alanine crystal has more NLO efficiency than that of pure L-alanine sample.

Measurement of dielectric parameters

The important dielectric parameters are dielectric constant and dielectric loss factor which reveal the electric properties of the insulating samples. For the measurement of dielectric constant and dielectric loss, the crystal was cut and polished. Good quality graphite paint was coated on the faces of crystal for the good ohmic contact. The graphite paint-electroded crystal was placed between the silver electrodes of the two-probe arrangement. An LCR meter (Agilent 4284A model) was used to measure capacity of the sample and hence dielectric constant was calculated using relation $\varepsilon_r = C/C_o$ where C_o is the capacity of the condenser without sample and C is the capacity of the condenser with sample. The dielectric loss (tan δ) was measured directly from the LCR meter. The variations of dielectric constant and dielectric loss (tan δ) of the grown crystals with different frequencies are displayed in the figures 3 and 4. It is noticed from the figures that dielectric constant and loss factor decrease with increase in frequency. The dielectric constant of an insulating sample is known to consist of contributions from electronic, ionic, dipolar and space charge polarizations, each dominating in a particular frequency range. The high value of dielectric constant at lower frequency is due to the space charge polarization. The low values of dielectric loss of the samples indicate that the rown crystals are of good quality dielectric materials [11].

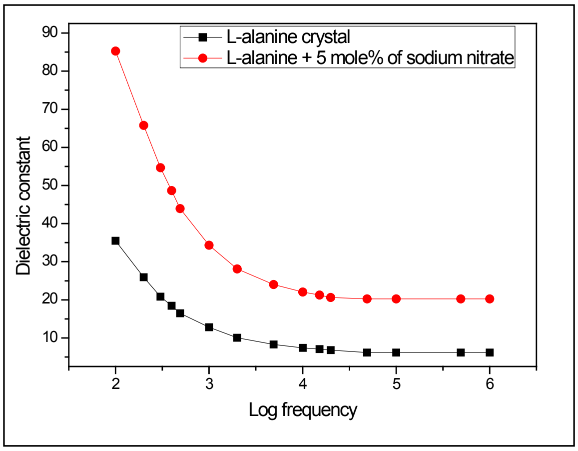


Fig.3: Frequency dependence of dielectric constant for pure and sodium nitrate doped L-alanine crystals at room temperature (30 °C)

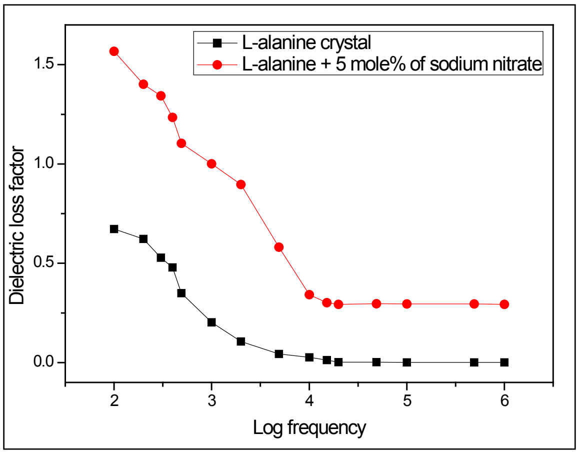


Fig.4: Frequency dependence of dielectric loss factor for pure and sodium nitrate doped L-alanine crystals at room temperature

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