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ORIGINAL ARTICLE

Effect of KDP on the growth, thermal and optical properties of L-alanine single crystals

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Abstract Non linear optical single crystals of L-alanine have been grown from aqueous solution of potassium di hydrogen phosphate (KDP) by the slow evaporation method. Single crystal X-ray diffraction confirms the orthorhombic structure of the grown crystals. Fourier transform infrared (FT-IR) studies reveal the presence of functional groups present in the grown crystal. The optical transmission study reveals very good transparency of the crystal and its optical band gap is found to be 4.9 eV. The thermal stability of the grown crystal is found to be 288.7 °C. The second harmonic generation (SHG) of the material was investigated using pulsed Nd: YAG laser. Third order non linear studies were performed using the single beam *Z*-scan technique using continuous wave Nd: YAG laser. Closed aperture *Z*-scan studies reveal negative nonlinearity in the crystals and open aperture *Z*-scan reveals saturation absorption. Also nonlinear parameter values such as nonlinear refractive index n_2, absorption coefficient β and nonlinear optical susceptibility $\chi^{(3)}$ were evaluated for the L-alanine crystal.

1. Introduction

Material with large second order optical nonlinearities finds wide application in the field of laser technology, laser communication, data storage technology and optoelectronic technologies frequency doubling, optical modulation (Meera et al., 2004; Ambujam et al., 2006; Heanue et al., 1994; Kang et al., 1990). Organic materials show good second harmonic generation (SHG) efficiency compared to inorganic materials (AnbuchudarAzhagan and Ganesan, 2012). Crystals of the amino acid family have been grown and studied by several researchers for their excellent nonlinear optical (NLO) properties (Liu et al., 2007; Zhang et al., 2008; Hernandez-Paredes et al., 2007; Eimerl et al., 1989). The L-alanine can be considered as the fundamental building block of more complex amino acids which shows strong nonlinear behaviour and abnormal phonon connection and is a system exhibiting vibra-

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tional solutions (Marder et al., 1991; Arun and Jayalakshmi, 2009). In the present work, single crystals of L-alanine have been grown from the mixture of alanine and potassium di hydrogen phosphate in the aqueous solution by the slow evaporation technique for the first time. The grown crystals were subjected to various characterization studies such as single crystal X-ray diffraction, FTIR analysis, UV–visible spectrum thermal studies and NLO test. Third order nonlinear studies were done using the *Z*-scan technique using continuous wave Nd: YAG Laser.

2. Experimental procedure

The title compound L-alanine was synthesized by taking AR grade L-alanine and AR grade potassium di hydrogen phosphate in the molar ratio of 1:1 and dissolved in deionized water. All starting materials were of AR grade and the growth process was carried out in aqueous solution. The solution is stirred well for 5 h. to obtain a homogeneous mixture. The resulting solution was filtered using Whatmann filter paper and it is kept in an undisturbed condition. The solution was taken in a beaker and closed with a perforated cover and kept in a dust free atmosphere. The crystals were harvested when they attained an optimal size and shape within 20 days. Optically transparent and defect free crystals were of dimensions $13 \times 8 \times 3\ mm^3$ and the photograph of the grown crystal is shown in Fig. 1.

3. Results and discussion

3.1. Single crystal X-ray diffraction

Single crystal X-ray diffraction analysis was carried out using a Bruker AXS diffractometer with MoKα ($\lambda = 0.7170$ Å) radiation to identify the lattice parameters. The single crystal X-ray diffraction studies confirm the orthorhombic structure with the space group of $P2_12_12_1$. The lattice parameters of L-alanine are; $a = 5.773$ Å, $b = 6.008$ Å, $c = 12.346$ Å, with volume $V = 428.1$ Å^3. The crystal parameters and cell volume were found to be well in agreement with reported values (Misoguti et al., 1996).

3.2. FT-IR spectrum studies

The middle infrared FTIR spectrum of grown L-alanine crystals was recorded in solid state using KBr pellet techniques. Dispersion was recorded using Perkin–Elmer Spectrum-one FT-IR spectrometer (Fig. 2). Absorption peaks at 3085.89, 1620.09, and 1513.37 cm^{-1} indicate the presence of NH_3^+ amine group and OH group of water molecules in the grown crystal (Lucia Rose et al., 2011). The spectrum exhibited a characteristic N–H stretching absorption band in the high frequency range between 2782 and 3088 cm^{-1}. The peak at 2782 cm^{-1} is attributed to C–H stretching mode vibration (Silverstein et al., 1981). The peak at 2111.0 cm^{-1}, in the overtone region is assigned to combinational and asymmetrical bending vibrations of NH_3^+. Very strong band occurring at 539 cm^{-1} is contributed of HO–P–OH bending vibration (Balamurugan and Ramasamy, 2009). The bending modes of CH_3 are positioned at 1316 and 1455 cm^{-1}, respectively. The peaks at 1113 cm^{-1} are due to C–O stretch and O–H bend of the CO–OH group is observed at 1236, 1306 and 1361 cm^{-1}, respectively. (Justin Raj and Jerome Das, 2007).

3.3. Transmittance spectral studies

The transmission spectrum was recorded at room temperature using Shimadzu 1601 UV–Vis–NIR spectrophotometer in the range of 190–1200 nm. The crystal is highly transparent in the entire visible region, whereas it has a UV cutoff at 256. The transmission is uniformly high (73%) for light in the visible region of electromagnetic spectrum, which is useful for nonlinear device application. The resultant spectrum is shown in Fig. 3. The optical band gap is obtained by plotting the graph between $h\upsilon$ and $(ah\upsilon)^2$ as shown in Fig. 4. From the graph, the optical energy gap of L-alanine is determined as 4.9 eV.

3.4. Thermal studies

The thermo gravimetric analysis of L-alanine crystals was carried out for the sample weight of 8.23 mg between 50 and 800 °C at a heating rate of 20 K min^{-1} in nitrogen atmosphere

Figure 1 Photograph of as grown crystal of L-alanine.

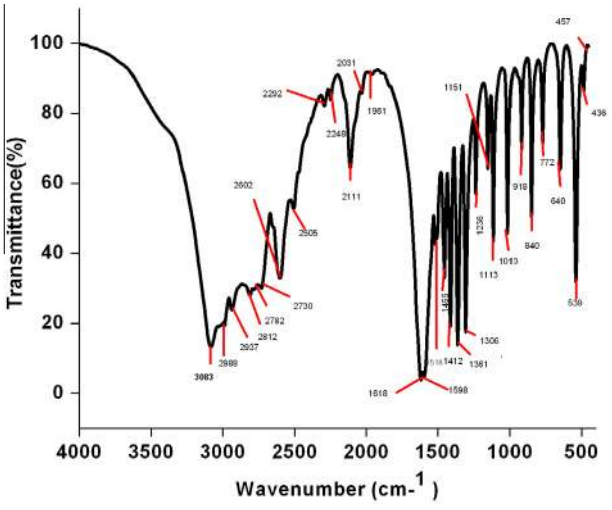

Figure 2 FT-IR spectrum studies of L-alanine crystal.

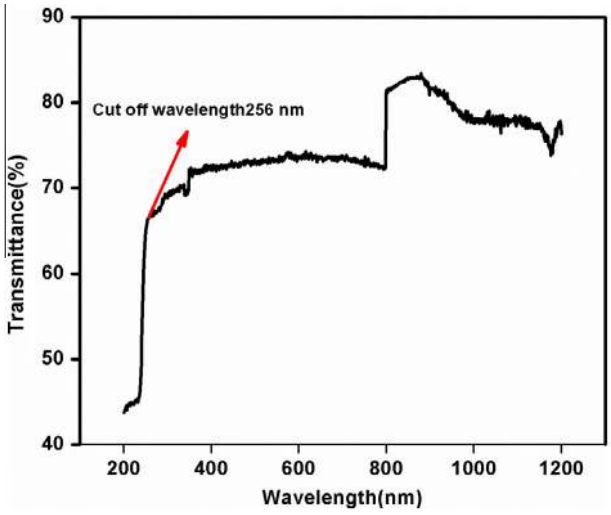

Figure 3 UV–Vis-NIR spectrum of L-alanine crystal.

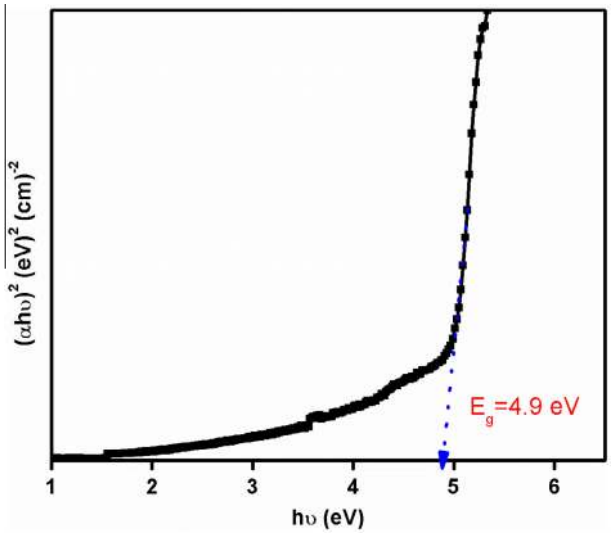

Figure 4 Plot of hυ and $(\alpha h\upsilon)^2$ for L-alanine crystal.

using NETZSCH STA 409 C/CD thermal analyser and the resultant spectrum is shown in Fig. 5. The TGA curve shows that there is no weight loss up to 220 °C and there is weight loss of about 1.40% of the initial mass at 229.2 °C. The maximum weight loss 96.239% is observed in the temperature range of 230–305 °C and hence the sample is found to be thermally stable and suitable for device applications. From DTA curve, it is observed that there is one endothermic peak at 288.7 °C which represents the decomposition of L-alanine. From this, it is concluded that the crystal melted only at 288.7 °C. The sharpness of this endothermic peak shows the good degree of crystallinity of the sample (HajaHameed et al., 2008).

3.5. Second harmonic generation (SHG) study

The SHG efficiency of L-alanine has been measured by the Kurtz and perry powder technique (Kurtz and Perry, 1968). A Q-switched solid state Nd: YAG laser (λ = 1064 nm) with a pulsed duration of 6 ns and frequency repetition rate of 10 Hz was used into the powder samples. The grown single crystals of L-alanine were ground into fine powder with uniform particle size and then filled into the micro capillary tube. The emission of bright green radiation (λ = 532 nm) from the crystals confirms the generation of second harmonics. The second harmonic signal of 9.0 mJ was obtained for an input energy of 0.68 J. The SHG value of potassium di hydrogen phosphate (KDP) crystal gives a signal of 8.8 mJ/pulse for the same input energy. Thus it is observed that the SHG efficiency of the L-alanine is 1.022 times than that of the standard KDP crystal.

3.6. Third harmonic optical studies

Z-scan experiments were performed using a 532-nm diode-pumped Nd: YAG laser beam (Coherent Compass™215 M-50), which was focused by a 3.5 cm focal length lens. The laser beam waist ω_0 at the focus is measured to be 15.84 μm and the Rayleigh length is 1.48 mm. The schematic of the experimental setup used is shown in Fig. 6. A 1 mm wide optical cell containing the sample in solvent is translated across the focal region along the axial direction that is the direction of the propagation laser beam. The transmission of the beam through an aperture placed in the far field is measured using a photo detector fed to the digital power metre (Field master Gs-coherent). For an open aperture *Z*-scan, a lens to collect the entire laser beam transmitted through the sample replaced the aperture. Development of high power laser sources has motivated an extensive research in the study of nonlinear optical properties and optical limiting behaviour of materials (Monaco et al., 1987; Johan kiran et al., 2007). The *Z*-scan technique developed by Sheik-Bahae et al. is used to characterize the nonlinear optical properties of the materials (Sheik-Bahae et al., 1989, 1990). This method is a simple and effective tool for determining the nonlinear properties. It has been used widely in material magnitudes of the real and imaginary parts of the nonlinear susceptibility, but also the sign of the real part. Figs. 7 and 8 show the open and closed aperture *Z*-scan curves for L-alanine crystal. In the closed aperture *Z*-scan curve, the pre-focal transmittance peak is followed by the post focal valley, which is the signature of negative nonlinearity (Shettigar et al., 2007), i.e. self-defocusing. The self-defocusing effect is due to the local variation of the refractive index with temperature. The measurable quantity ΔT_{p-v} can be defined as the difference between the normalized peak and valley transmittances, $T_p - T_v$. The variation of this quantity as a function of $|\Delta\varphi_0|$ is given by

$$\Delta T_{p-v} = 0.406\ (1-S)^{0.25}|\Delta\varphi_0| \quad (1)$$

where $S = 1 - \exp(-r_a^2/\omega_a^2)$ is the aperture linear transmittance (0.01), $\Delta\varphi_0$ is the on-axis phase shift. The on-axis phase shift is related to the third-order nonlinear refractive index by

$$\Delta\varphi 0 = k n_2\ L_{\text{eff}} I_0 \quad (2)$$

where $k = 2\pi/\lambda$, $L_{\text{eff}} = [1 - \exp(-\alpha L)]/\alpha$ is the effective thickness of the sample, α is the linear absorption coefficient, L the thickness of the sample, I_0 the on-axis irradiance at focus and n_2 the third-order nonlinear refractive index.

Generally the measurements of the normalized transmittance versus sample position, for the cases of closed and open aperture, allow determination of n_2 the nonlinear refractive in-

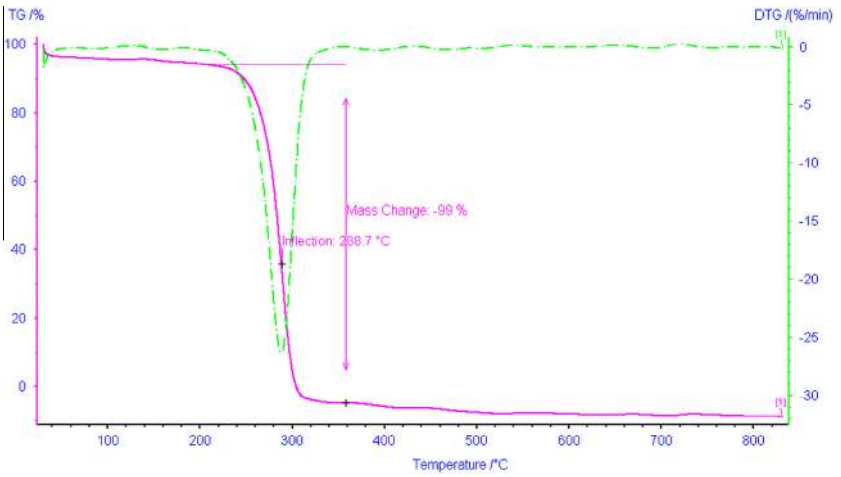

Figure 5 TG/DTA curve for L-alanine crystal.

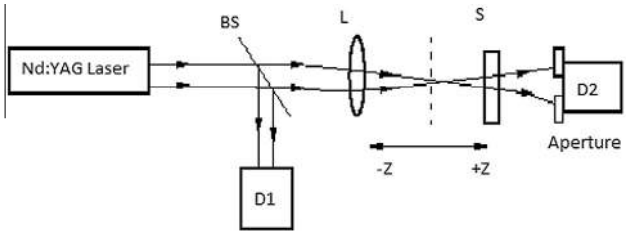

Figure 6 Schematic of experimental arrangement for the *Z*-scan measurement.

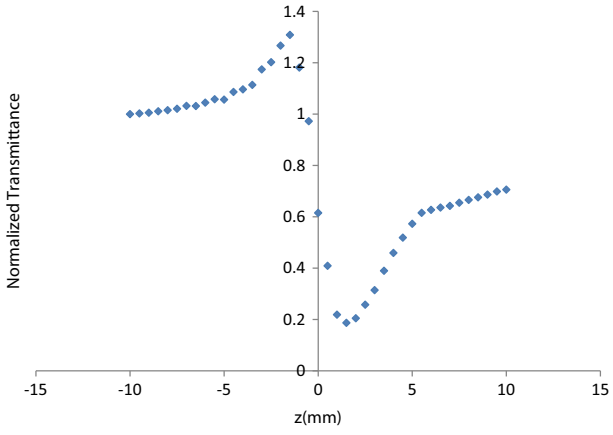

Figure 7 Closed aperture curve scan ($s = 0.035$) of L-alanine crystal.

dex and the SA coefficient β. Here, since the closed aperture transmittance is affected by the nonlinear refraction and absorption, the determination of n_2 is less straightforward from the closed aperture scans. Therefore, it is necessary to separate the effect of nonlinear refraction from that of the nonlinear absorption. A simple and approximate method to obtain purely effective n_2 is to divide the closed aperture transmittance by the corresponding open aperture scans representing such plots obtained for the samples, i.e., the ratio of closed aperture and the open aperture *Z*-scans as shown in Fig 9.

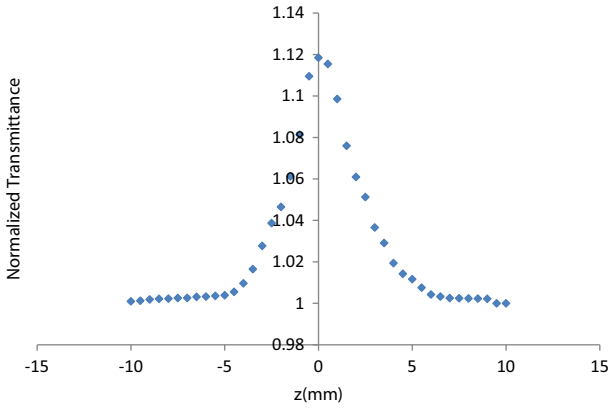

Figure 8 Open aperture curve ($s = 1$)for L-alanine n crystal.

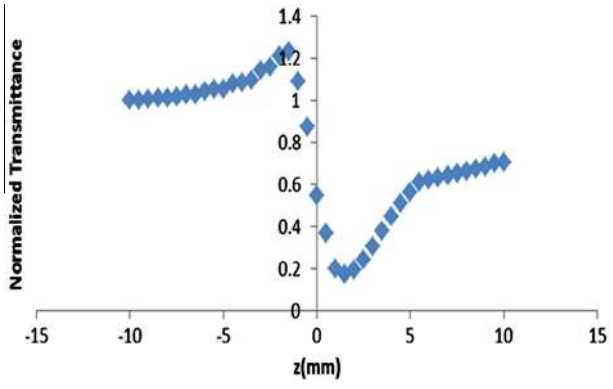

Figure 9 Ratio curve for L-alanine crystal.

Table 1 Non-linear optical parameter.

Compound	$n_2 \times 10^{-8}$ (cm^2/W)	$\beta \times 10^{-4}$ (cm/W)	$\chi^{(3)} \times 10^{-6}$ esu
L-alanine	8.82	0.15	4.31

The data obtained in this way reflect purely the effects of nonlinear refraction.

The nonlinear absorption coefficient β can be estimated from the open aperture Z-scan data. The normalized transmittance for the open aperture condition is given

$$T(Z, S = 1) = [-q_o(z)m]/(m+1)^{3/2} \quad (3)$$

For $q_0(0) < 1$, where $q_0(z) = \beta I_0 L_{\text{eff}}/(1 + z^2/z_R{}^2)$, $z_R = k\omega_0{}^2/2$ is the diffraction length of the beam and ω_0 is the beam waist radius at the focal point and $k = 2\pi/\lambda$ is the wave vector.

The experimental measurements of n_2 and β allow one to determine the real and imaginary parts of the third-order nonlinear optical susceptibility $\chi^{(3)}$ according to the following relations

$$R_e\chi^3(\text{esu}) = 10^{-4}\varepsilon_0 c^2 n_0^2 n^2/\pi(\text{cm}^2/\text{W}) \quad (4)$$

where $\in_0$ is the vacuum permittivity, and c the light velocity in vacuum:

$$\text{Im}\chi^3(\text{esu}) = 10^{-2}\varepsilon_0 c^2 n_0^2 \lambda\beta/4\pi^2(\text{cm/W}) \quad (5)$$

The absolute value of $\chi^{(3)}$ is calculated from $|\chi^{(3)}| = [(\text{Re}(\chi^{(3)}))^2 + (\text{Im}(\chi^{(3)}))^2]^{1/2}$

Nonlinear parameters such as nonlinear refractive index n_2, nonlinear absorption coefficient β, and nonlinear susceptibility χ, have been evaluated and tabulated in Table 1. Both NLA and NLR contribute to the third-order nonlinearity of the sample.

4. Conclusion

Single crystals of L-alanine have been grown from aqueous solution of potassium di hydrogen phosphate (KDP) by the slow evaporation method. The single crystal X-ray diffraction studies confirm that title crystal belongs to the orthorhombic structure with the space group $P2_12_12_1$. The presence of functional groups was determined using FTIR analysis. UV–visible-NIR Spectrum of L-alanine shows 73% transparency in visible region and its band gap energy is found to be 4.9 eV. The grown crystals are thermally stable up to 288.7 °C. The SHG efficiency of the L-alanine is 1.022 times than that of the standard KDP crystal. The Z-scan measurements further confirm that the material exhibits large third order nonlinear optical properties. The third order nonlinear parameters are highly encouraging for the crystal. All these studies indicate that the grown crystal is the potential material for second harmonic as well as third harmonic generation applications.

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