Opto-electronic study, NLO investigation and antimicrobial activity analysis on L-alanine doped Ethylene Diamine Tetra Acetate composite crystal

M. Joice Malini,[1&2] R.Kunjitham[1] M.K.Sangeetha[2], R.Arumugam[3]

*[*1]Department of Chemistry, Poombuhar college (Autonomous), Melaiyur, Tamilnadu, India.*

[2]A.V.C. College of Engineering, Mayiladuthurai, Tamilnadu, India.

[3]Department of Botony, A.V.C. College, Mayiladuthurai, Tamilnadu, India.

Affiliated to Bharathidasan University, Tiruchirappalli, Tamilnadu, India.

ABSTRACT

Optically transparent single crystal; L-Alanine doped EDTA is fruitfully grown using slow evaporation technique at room temperature. The grown crystals have been characterized morphologically, analyzed spectroscopically and thereby crystal and structural properties have been interpreted. The crystal parameters have been calculated from experimentally observed data and the calculated values proved orthorhombic crystal lattice formation. The variable refractive indices for different coordinates were measured and it ensured birefringence effect in the crystal. Thermal properties were studied from the data observed from TGA and DSC instruments and thermal stability of the sample was validated. The structural and morphological influence of L-Alanine on EDTA was analyzed by SEM. The partial organic compositions were identified from EDAX peaks and the percentage of organic elements in the crystal was traced. The NLO arrangement in the molecular configuration was mapped and SHG test was made to prove the NLO activity. The Micro dilution bioassay method described by ELOFF was followed to found the Minimum inhibitory concentration (MIC) of LVE for antibacterial activity.

Keywords: crystal growth, birefringence effect, NLO activity, TGA, DSC and MIC.

1. Introduction

The ideal organic crystal material could have potential applications in non-linear optical (NLO) devices and that should possess the combination of large non-linear figure of merit for frequency conversion, high laser damage threshold, fast optical response time, wide phase matchable angle, architectural flexibility for molecular design and morphology, optical transparency and high mechanical strength [1-4]. Compared with inorganic NLO materials, organic composite materials confidently fulfill the requirements needed to acquire enriched NLO activity. By adopting suitable energetic compound to organic materials, the environmental stability, chemical and mechanical stability, laser damage thresholds and phase matching properties can be enhanced [5-7]. In this way, the fabrication of crystals with semi organic composite have some advantages such as higher second order optical non-linearities, short transparency cut-off wavelength and stable physico-chemical performance over the traditional inorganic and organic crystals [8-9].

In order to get greater Second Harmonic Generation (SHG) efficiency, the organic compound requires highly Polarizable σ and π bonding molecular systems possessed asymmetric charge distribution [10-11]. Since there is a large demand for organic crystals in electronic industries in present time, it is required to synthesize new NLO materials and improve the properties of the existing materials. In this work, the growth and characterization of EDTA doped L-Alanine crystals by slow evaporation technique are reported, as no reports are available in literature. Hereafter, the grown semi organic crystals will be named as LAE (L-Alanine doped EDTA). In this work, the results of new L-Alanine EDTA crystals for the first time along with the characterization and analysis studies on Antibacterial activity.

2. Experimental Technique

The Selection of the solvent is an important step in the growth of crystals from solution by slow evaporation method. In this method, water is used as a solvent for dissolving organic substance. Commercially available annular grade L-alanine and disodium salt of EDTA were used in equal-molar ratio for the Crystal growth. Initially, the material was purified by repeated re-crystallization then, the saturated solutions of L-alanine and EDTA at room temperature were prepared. Then the solution is filtered. The filtered solution was taken in a beaker which was sealed with small size hole to control the evaporation of the solvent. The well-defined crystals are obtained within a period of 15 days. White transparent single crystals of Pure L-Alanine and doped LAE crystals are harvested and are shown in within Table 1.

2.1. Recording details

The grown raw crystal composite was fashioned up regarding its optical axis and it was permitted to clean and to be characterized. The XRD pattern was documented for raw sample of present case and the clear XRD pattern was determined for the analysis.

3. Results and discussion

3.1. Powder XRD analysis

The crystallinity nature of the studied organic composite was proved by obtained XRD spectrum with Cu K α (λ = 1.5418 A°) radiation. The sharp peak with maximum intensity showed the measure of better arrangement of interplanes of crystalline which explicit the optimized molecular configurational setup. The XRD pattern for showing different interplane reflections for LAE are shown in the Figure 1. According to the XRD peak assignment, the reflection-signals have been recorded at 21°, 28°, 29°, 34°, 38°, 46° and

55° for (001), (020), (002), (121), (220) and (301) miller indexed planes and they confirmed the orthorhombic crystal lattice existed in present crystal. In the case of organic composite, the peak intensity is usually weak and it always showed defective crystal formation and inactive crystallinity [15]. But, in this case, the peaks were observed with strong intensity that illustrates very good crystal arrangement. Due to this condition, the crystal was found to be formatted in good order and interplanes were spaced in good order. By the better configuration existed in organic crystal, the space group was clearly found to be $P2_1$ $P2_1$ $P2_1$[16]. For understanding the crystal with expected dimensions, the crystal parameters were determined in order and they found to be a=6.023 Å, b=12.343 Å and c=5.784 Å and crystal dimension was α= β= γ=90°. All such parametric values proved orthorhombic structure of crystal.

The volume of unit cell usually mention packing fraction capacity of crystals and it was found to be 430 $Å^3$ which was moderate and able to make high dense packing in the crystal. The Birefringence effect was measured to be 0.188, it was moderately high to produce ordinary and extraordinary optical rays when it is hitting. The NLO efficiency was estimated with respect to SiO_2 and it was 0.6361. This was clearly showed the moderate NLO process taking place over the crystal material. The transmittance value was found to be 0.4500 – 2.317 μm for the present case. It belongs to beyond UV and within visible region of spectrum that denoted the optical response of the material. The complexity of crystal was calculated to be 381 which illustrates periodic network of atoms and bonds in molecular configuration and thereby unit cell of crystal. It was more than enough to appraise lattice periodicity of present crystal. Here, from the parameter analysis, it was found that, though, the L-Alanine was doped with EDTA, the L-Alanine base lattice was maintained and EDTA was retained in such lattice.

4.4. THERMAL ANALYSIS

Thermo gravimetric (TGA) and differential scanning calorimetric (DSC) analyses were carried out, using universal V4-5A-TA instrument at a heating rate of 20°C/min, recorded in the same chart are shown in Figure 2. Thermo gravimetric analysis (TGA) usually carried out to record the weight of a substance as a function of temperature. In the present case, the TGA and DSC are carried out between 20°C and 800°C in an inert environment. The weight, particle size and the mode of preparation (the pre-history) of a sample, all govern the thermo gravimetric results. In practice, a small sample weight is desirable for thermo gravimetric results and hence the weight of the sample taken for investigation is 6.123mg. In TGA, the endothermic peak at around 250°C represents the melting point of the sample. In figure 6, there are four distinct weight losses was found above 250°C. At the first stage, about 91.44% of weight loss produced at 253.15°C, at the second stage, there is 59.83% of weight loss taking place at 284.59°C,. At the third stage, 40.01% of weight loss occurs at 294.16°C. In the final step, there is 20.02% of sample violated at 308.48°C, leaving about 0.8489% of the sample as end residue around 515.10°C. The exothermic process is nearly Coincide with the TGA weight loss prediction.

The DSC is used to predict the phase transitions or chemical reactions can be followed by observation of the heat absorbed or liberated: Fusion, change in the crystalline state and other physical changes of the sample while heating give sharp endothermic peak. Dehydration is indicated by a broad endothermic peak. Certain chemical changes such as oxidative degradations are aided by exothermic peaks .The endothermic peak at 250°C is indicative of the melting point of the sample. From the above observation, it was clear that, the melting point of present crystal was found to be stabilized and elevated to high degree of temperature.

4.5. SEM observation

The surface of the present crystal was scanned at different magnification order and they are presented in Figure 3. Here, the crystal was customized by adopting L-Alanine organic molecule in EDTA molecular configuration and they crystallized by slow evaporation method. Different scanning pattern was registered in order to signify the smoothness of the surface and crystal grows ability. Here the Figure 3 (a) showed magnifications of 15kV and at a scale of 12.7µm where in which smoothed surfaces were found in the form of fine wire. In Figure 3(b), at magnifications of 15kV and at a scale of 63.6 µm, the joint network of fine wires. In Figure 3(c), at magnifications of 15kV and at a scale of 127 µm, well profound smoothness was found. In Figure 3(d), at magnifications of 15kV with scale of 25.4 µm, hairpin loop was appeared. From all SEM images, it was observed that, due to the addition of the doping species on dopant EDTA, the growth pattern is modified well and vertical and cross sectional layer growth is observed to be good and hence EDTA acts as a excellent growth catalyst.

4.6. EDAX examination

The partial energy distribution profile of present organic crystal composite was mapped from the EDAX spectrum and the dispersive elements are tabulated and are shown in Figure 4. The percentage of presence of organic elements is illustrated in same figure and also the atomic percentage was observed. The first organic element O was found to be 41.27 %, C was observed to be 34.63 % and N was calculated to be 14.90 %. All the organic elements are participated to customize the LAE crystal and it was verified with crystal parametric values. From the data, it was conferred that, the organic composite was pure and

no contamination was found. Except Na, the crystal is needed not to be optimized and energy dispersion was appeared to be normal and equal distribution rate.

4.7. SHG Efficiency Measurement

The SHG property of LAE is determined by the modified version of powder technique by Kurtz and Perry. The microscopic origin of non-linearity in the NLO materials is due to the presence of delocalized π-electron systems, degenerate donor and accepter groups, which enhance their asymmetric polarizability. Each type of constituent chemical bond is regarded as one part of the whole crystal that has contributions to the total non-linearity. The distribution of valence electrons of the metallic elements is an important factor that strongly affects the linear and nonlinear properties of each type of constituent chemical bond. The fundamental beam of 1064 nm from Q-switched Nd:YAG laser was used to test the SHG property of the grown crystal. The input pulse with energy 1.2mJ pulse and pulse width of 10 ns with a repetition rate of 10 Hz was used. The fundamental beam was filtered by using IR filter. A photo multiplier tube (Philips photonics) was used as detector of the optical output signal emitted by the sample. Potassium dihydrogen ortho phosphate (KDP) [50 mV] was used as the reference material. The second harmonic generation was confirmed by the emission of green light having the wavelength around 532 nm and the output is 60 mV and hereby the NLO efficiency was proved.

4. Conclusion

L-Alanine was doped with EDTA and the corresponding crystal was grown using slow evaporation method. The crystal was found to be very acute and pure and the crystal physical-evaluation determined that the grown crystal was highly transparent and is able to act as NLO material. The XRD parameters were estimated and the respective data was calculated from the standard formula. The XRD morphological observation was made and

calculated data confirms the orthorhombic lattice formation in the crystal and has taken the effect of NLO activity. The refractive indices for different coordinates ensured that, the entered optical energy was found to be boosted with higher order which was different in different crystal planes. In order to evaluate the NLO activity, the gain of amplification was measured and observed that the efficiency was comparatively high. The SEM images was examined with respect to step-up magnification process, the corresponding surface view of molecular arrangements have been identified.

References

[1] H. O. Marcy, L. F. Warren, M. S. Webb, C. A. Ebbers, S. P. Velsko, G. C. Kennedy and G. C. Catella, Applied Optics, Vol. 31, No. 24, 1992, pp. 5051-5060.

[2] Y. J. Ding, X. Mu and X. Gu, Nonlinear Optical Phy- sics and Material, Vol. 9, No. 1, 2000, p. 21.

[3] X. Q. Wang, D. Xu, D. R. Yuan, Y. P. Tian, W. T. Yu, S. Y. Sun, Z. H. Yang, Q. Fang, M. K. Lu, Y. X. Yan, F. Q. Meng, S. Y. Guo, G. H. Zhang and M. H. Jiang, Material Re-search Bulletin, Vol. 34, No. 12-13, 1999, pp. 2003-2011.

[4] L. Li, Z. P. Wang, G. R. Tian, X. Y. Song and S. X. Sun, Journal of Crystal Growth, Vol. 310, No. 6, 2008, pp. 1202- 1205.

[5] G. Pasupathi and P. Philominathan, Material Letters, Vol. 62, No. 28, 2008, pp. 4386-4388.

[6] M. N. Bahat and S. M. Dharma Prakash, Journal of Crystal Grow- th, Vol. 236, No. 1-3, 2002, pp. 376-380.

[7] X. Ren, D. L. Xu and D. F. Xue, Journal of Crystal Growth, Vol. 310, No. 7-9, 2008, pp. 2005-2009.

[8] N. J. Long, “Organometallic Compounds for Nonlinear Optics, The Search for Enlightenment,” Angewandte Chemie, Vol. 34, No. 1, 1995, pp. 21-38.

[9] K. Y. Li, X. T. Wang, F. F. Zhang and D. F. Xue, Physical Review Letters, Vol. 100, No. 23, 2008, pp. 659-666.

[10] D. F. Xue, L. J. Zou, L. Wang and X. X. Yan, Modern Physics Let-ters B, Vol. 23, No. 31-32, 2009, pp. 3761-3768.

[11] P. Groth, “Chemische Krystallographie,” Verlag Wilhelm Engelmann, Leipzig, Vol. 2, 1908, 362.

Table 1: Crystal parameters of L-Alanine doped EDTA

S. No.	Parameters	Values	Crystal view
1	**Space group**	$P2_1$ $P2_1$ $P2_1$	
2	**Unit cell**		
	a	6.023 Å	
	b	12.343 Å	
	c	5.784 Å	
3	**α= β= γ**	90°	
4	**Crystal type**	Orthorhombic	
5	**Refractive index**		
	n_1	1.58	
	n_2	1.76	
	n_3	1.65	
6	**Volume**	430 $Å^3$	
7	**Birefringence (Δn) Kλ/t**	0.188	
8	**NLO efficiency**	0.6361 [I/I(SiO_2)]	
9	**Transmittance**	0.4500 – 2.317 µm	
10	**complexity**	381	

Figure 1: XRD spectral pattern of LAE crystal

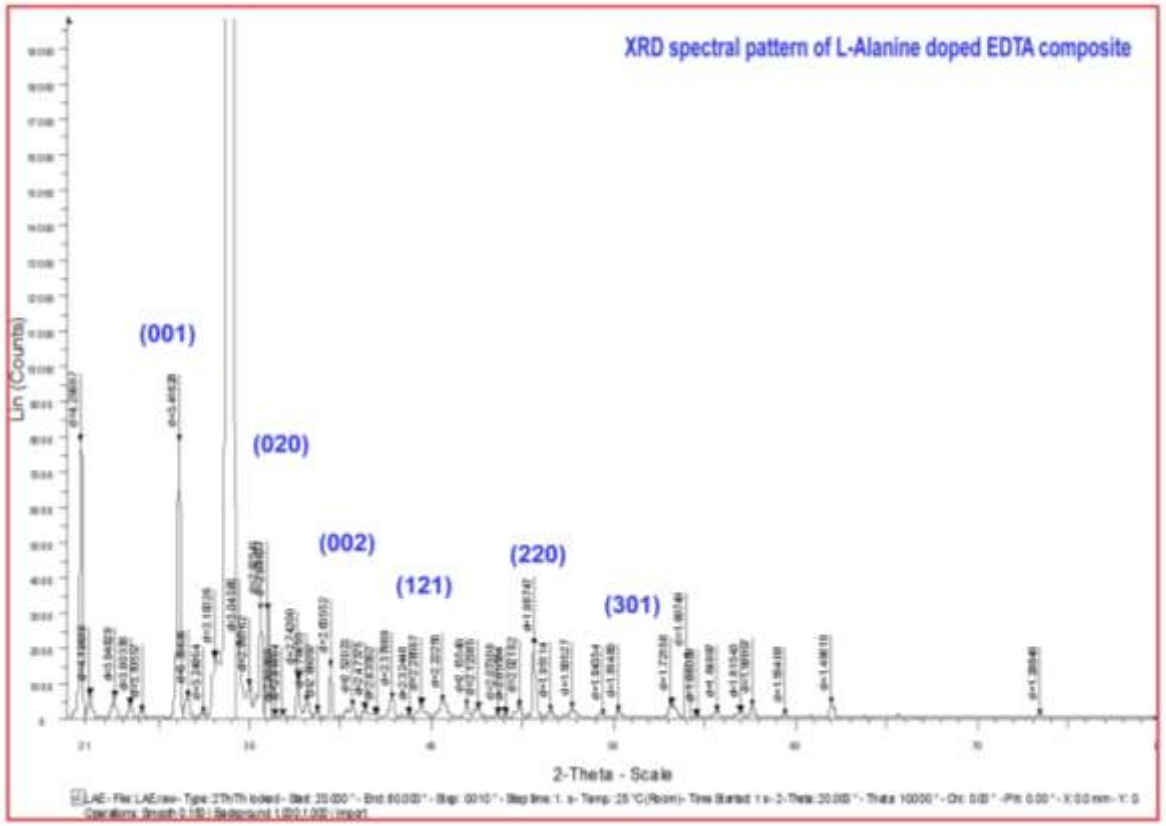


Figure 2: Thermal analysis curve

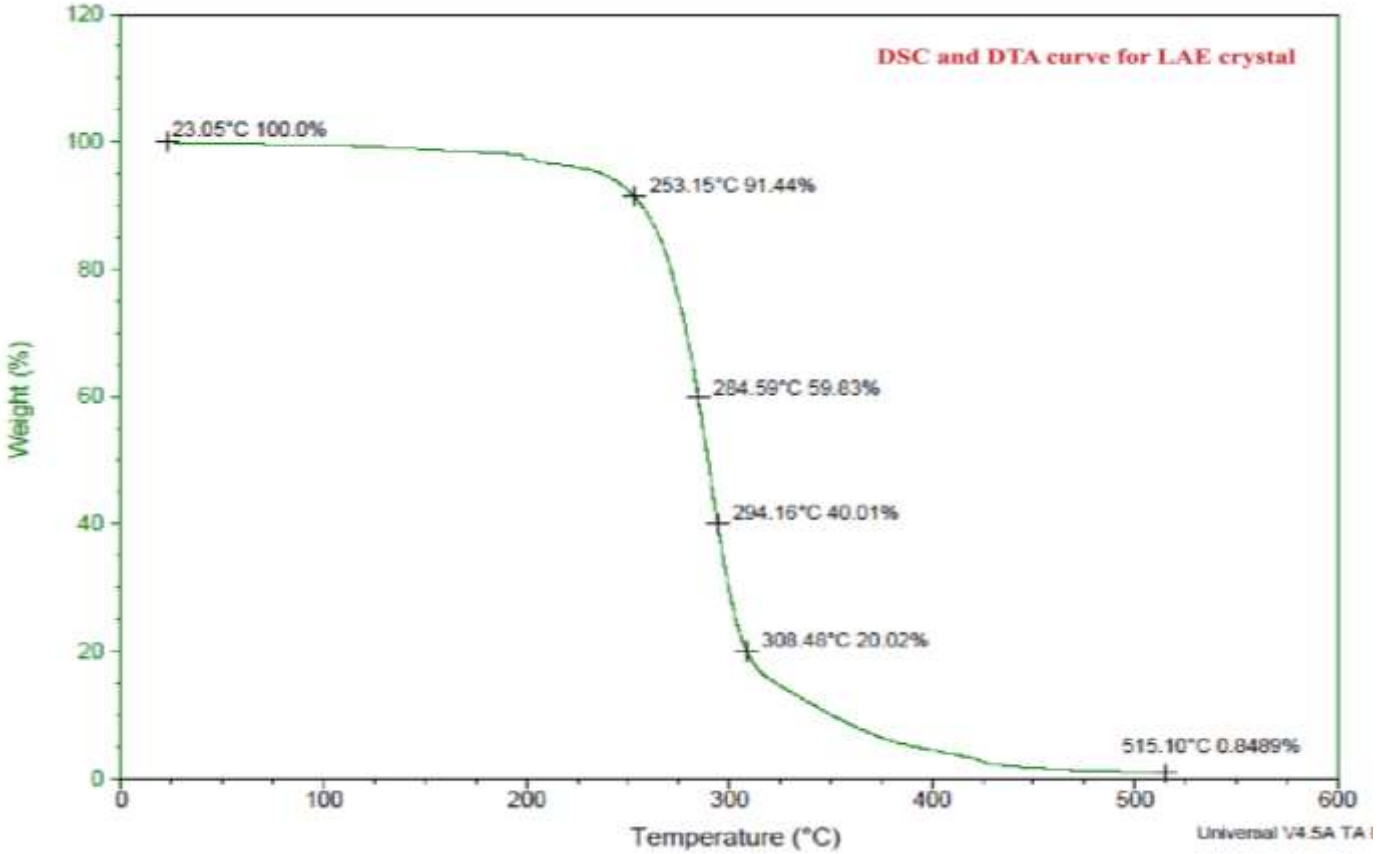
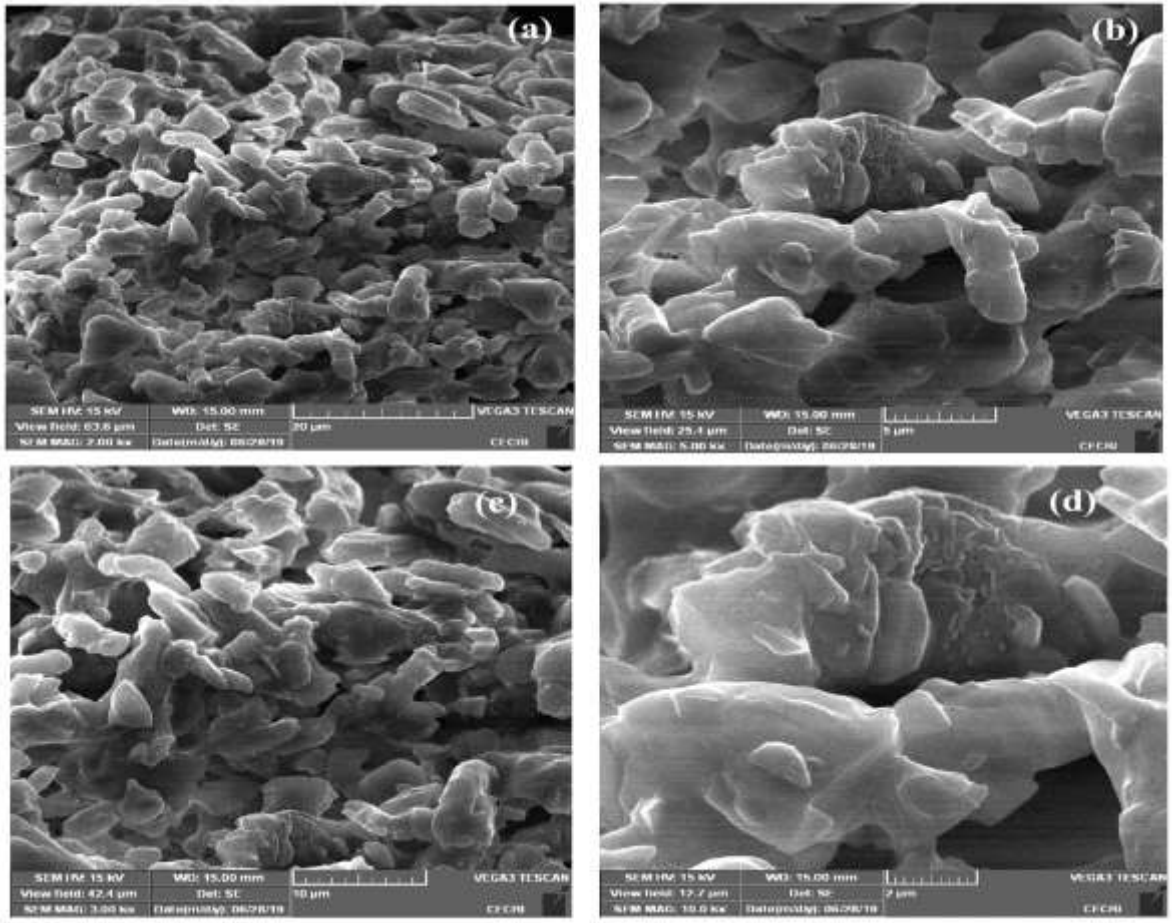


Figure 3: SEM images of LAE crystal



Figurer 4: EDAX examination spectrum

Element	*Spectral type*	*Element %*	*Atomic %*
O	*ED*	*41.27*	*37.24*
C	*ED*	*34.63*	*41.62*
N	*ED*	*14.90*	*15.36*
Na	*ED*	*9.20*	*5.78*
Total		*100*	*100*