

A Review of the L-Alanine and Its Doped Forms to Study Its Structural, Optical and 2nd Order SHG Related Properties

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Abstract

L-Alanine is one of the members of amino acids family [1] having excellent SHG related properties to be used in nonlinear optical applications. In the present study, we review the structural, optical and 2nd order SHG related properties of solution grown L-Alanine and its doped forms. XRD analysis reports the noncentrosymmetric, orthorhombic structure of LA single crystals and no change in its basic structure is observed upon doping with materials like HCl, CdBr₂, Li₂SO₄, Co²⁺ etc. except in the case LA is doped with HNO₃, CdCl₂, Bi(NO₃)₃ and C₆H₃N₃O₇ in which LA admixed forms was found to be having monoclinic structure. Zwitterionic structure of LA and its doped forms was confirmed by the FTIR spectral analysis. Low value of dielectric loss for LA and its doped forms at high frequencies depicts the enhanced optical quality and efficiency and hence is a very much suitable parameter in view of the second harmonic generation coefficient. UV-Vis investigation reports high transparency of LA crystals in UV region. Doping with other materials as given above further causes enhancement in the transparency ratio. An enhancement in the value of SHG efficiency is seen in case of LA single crystals (in doped form) as compared to LA single crystals (in pure form having SHG efficiency 0.33 times of KDP used as reference material) except for L-Alanine cadmium chloride enhancing its suitability to be used in NLO applications. In this review paper, we have also discussed the comments proposed by some of researchers on the novel formation of new NLO materials as L-Alanine compounds by chemically reacting L-Alanine with other materials viz., cadmium bromide, C₆H₃N₃O₇ (picric acid) etc.

Keywords: L-Alanine; Solution grown; NLO properties

Introduction

Enormous research work has been done on amino acids, a class of materials with promising physical and optical properties making it a potential candidate to be used in non-linear optical applications. Different amino acids find very much suitability in the wide areas of photonics and optoelectronics. L-Alanine having molecular formula CH₃CHNH₂COOH is the smallest one molecule among all classes of organic amino acids [1]. As per this review report, its second order harmonic generation efficiency is 0.33 times than that of KDP. In the present review paper, intention is focused to summarize the preparation of L-Alanine and its different doped forms by solution grown technique and comparing their optical and

structural properties as well suitability to use in NLO applications by measuring their second order harmonic generation efficiency. Review of complexes of L-Alanine with different inorganic salts synthesized by solution grown method have also been done and showed enhanced value of second order harmonic generation efficiency. High value of electronic polarisibility of amino acids makes them potential candidates to be used in non-linear optical applications like high density data storage, optical computational purpose as well as spectroscopy related applications.

This paper reviews the extensive investigation of amino acids (in its pure as well as doped form) like L-Alanine, CdCl₂ doped L-Alanine, CdBr₂ doped L-Alanine, Lithium sulphate admixed L-Alanine, HCl added L-Alanine, Co²⁺ doped L-Alanine, LAAN with chemical formula C₃H₇NO₂⁻ C₃H₈NO₂⁺ NO₃ and L-Alanine Alanine picrate monohydrate to note the structural, optical and NLO application based properties of LA and effect of doping with inorganic materials on these properties.

Preparation of crystals

In the reported data, Solution grown technique was employed by different researchers to prepare the single crystals of pure LA and its doped form. In this method, Saturated solution of LA and its doped form is allowed to get supersaturated either by gradual lowering of its temperature or by allowing the slow evaporation of the solvent in order to grow crystals of the solute raw material.

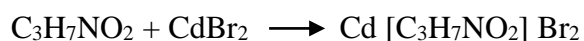
M.L. Caroline et.al. [2] in her paper prepared an 200 mL saturated aqueous solution of LA and allowed its cooling at rate of 0.1°C per day in order to obtain single crystals with high transparency and good morphology.

M.L. Caroline et.al. [3] in her other paper prepared Co²⁺ doped LA crystals using slow evaporation method in which Co²⁺ dopants with concentration of 5% were added to the LA aqueous solution. In the period of 2 weeks, crystals with well defined morphology and size 2.0 x 1.0 x 1.8 cm³ are obtained.

Fig.1 shows the good transparent single crystals of pure LA solution synthesized by N. Vijayan et.al. [4].

A. Aravindan et. al. [1] prepared good transparent LAAN crystals as shown in fig.2 by carrying out a chemical reaction between HNO₃ and dilute LA solution and subsequent repeated recrystallization was done in order to achieve desired purity of LAAN crystals during solution grown process.

P.Ilayabarathi et. al. [5] carried out the synthesis of LA cadmium bromide crystals by first adding the cadmium bromide aqueous solution with LA aqueous solution in 1: 1 stoichiometric ratio represented in below chemical reaction:



Solution prepared after going through uniform agitation using a magnetic stirrer was finally allowed to undergo solvent evaporation in order to obtain LACB well transparent single crystals.

Similarly, a homogeneous mixture of L-Alanine cadmium chloride solution was obtained by mixing Cadmium chloride (aq.) with LA (aq.) in 1: 1 stoichiometric ratio and was allowed to undergo solvent evaporation in order to obtain LACC well transparent single crystals as reported by P. Kalaiselvi et. al. [6].

S. Muhammad et. al. in his paper carried out the synthesis of LALAPM crystals [7] by solution grown technique by first adding L-Alanine and picric acid in stoichiometric ratio of 2: 1 as per the following chemical reaction:



The solution thus obtained was allowed to cool at 0.5°C per day for 4 days and then after initialization of nucleation among this, cooling rate was lowered to 0.15°C for final growth of crystals.

A comparison of different parameters employed during crystal synthesis and size of crystals obtained for above reported pure and doped LA single crystals is tabulated in table 1.

Table 1 for comparison in method of preparation

S. No	Crystals prepared	Method of preparation	Stoichiometric ratio (L-Alanine : doped material)	Size of crystals	Span during which crystals growth takes place	Author
1	L-Alanine	Solution growth	-----	1.7 x 0.8 cm ²	-----	N. Vijayan et. al.
2	Li ₂ SO ₄ doped L-Alanine	Solution growth	2:1	-----	-----	T. Vela et. al.
3	L-Alanine	Solution growth	1 (LA) :1 (KDP)	13 x 8 x 3 mm ³	20 days	T. Thilak et.al.
4	Bismuth nitrate doped LA crystals	Solution growth	-----	-----	30-40days	N. Suresh et. al.
5	HCl added L-Alanine	Solution growth	1 : 1	32 x 23 x 10 mm ³	40 days	M. Shkir et. al.
6	L-Alanine L-Alaninium picrate monohydrate	Solution growth	1 : 1	-----	20 days	S. Muhammad et. al.
			1.5 : 1			
			2 : 1			
7	L-Alanine	Solution growth	-----	1 x 1x 3 cm ³	-----	L. Misoguti et. al.
8	Co ²⁺ doped L-Alanine	Solution growth	5 wt % Co ²⁺ ions were added to the mother solution.	2 x 1 x 1.8 cm ³	14 days	M.L. Caroline et. al.
9	L-Alanine Cadmium Chloride	Solution growth	1 : 1	12 x 6 x 3 mm ³	75 days	P. Kalaiselvi et. al.
10	L-Alanine Cadmium Bromide	Solution growth	1 : 1	-----	-----	P. Ilayabarathi et. al.

11	L-Alanine	Solution growth	-----	2.4 x 1.2 x 1.6 cm ³	14 days	M.L. Caroline et. al.
12	L-Alanine L-alaninium nitrate	Solution growth	-----	1 x 1.3 x 1.2 cm ³	26 days	A. Aravindan et. al.



Fig 1 shows the pure LA crystal synthesized by N. Vijayan et.al. [4]

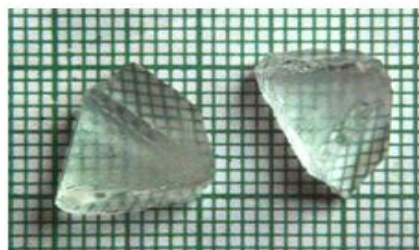


Fig 2 shows the LAAN crystals synthesized by A. Aravindan et. al. [1]

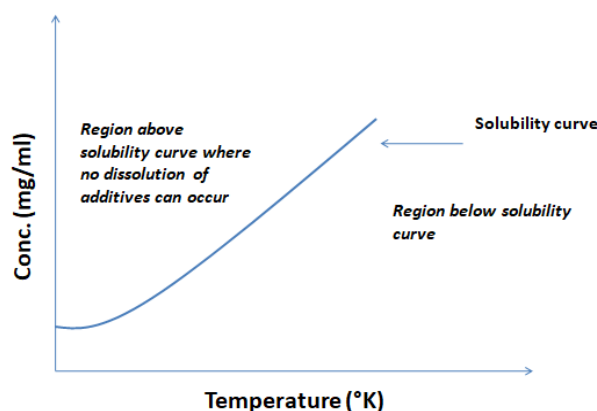
Solubility

Solubility of the given material plays crucial role in order to decide size of crystals to be prepared and its value is a function of temperature. Solubility of L-Alanine is usually observed to be increasing with increase in temperature [4] as reported by N. Vijayan et.al. wherein L-Alanine (solute) was dissolved in the de-ionized water (solvent). The solution was then continuously stirred at constant temperature to achieve complete dissolution and this process was then further repeated for different temperature in order to obtain solubility curve [4].

T. Vela et. al. also reported an increasing pattern of solubility curve with respect to temperature during solution grown synthesis of Lithium Sulphate admixed L-Alanine (LSLA) single crystals [8].

Similarly, S. Muhammad et. al. also prepared solubility curve for L-Alanine L-Alaninium picrate monohydrate (LALAPM) showing an increasing trend with respect to temperature [7].

Below graph 1 depicts a general trend for solubility curve for pure LA and some of its doped form as discussed above.



Graph 1 represents the general trend of solubility curve for LA and its doped forms.

XRD study

Using X-ray diffraction technique, Crystal structure, symmetry space group and lattice parameters of identified unit cell of L-Alanine prepared using solution growth technique were reviewed and comparison were studied among pure as well as doped form of L-Alanine crystals. X-ray diffraction study of pure L-Alanine single crystals were carried out by M.L. Caroline et.al. using Enraf Nonius CAD4 diffractometer in which Mo- K_{α} radiations were incident having wavelength 0.7170 \AA on the probe crystal. Orthorhombic type lattice possessing $P 2_1 2_1 2_1$ space group symmetry of the crystal with lattice parameters found to be having values $a= 6.0220 \text{ \AA}$, $b= 12.3230 \text{ \AA}$ and $c=5.7790 \text{ \AA}$ was reported. [2]

In her other paper, M.L. Caroline et.al. carried out a comparative study between pure and Co^{2+} ions doped L-Alanine single crystals. She reported increase in unit cell volume due to change in lattice parameters without any change in the crystal lattice type and its basic structure in the Co^{2+} ions doped L-Alanine single crystals [3].

N. Vijayan et. al.. also investigated the crystal structure of solution grown pure L-Alanine single crystals using this technique. Reports obtained from the powder X-ray diffractometer as reported by N. Vijayan et. al. also confirms the orthorhombic category of the L-Alanine crystal lattice with unit cell sides $a= 6.0320 \text{ \AA}$, $b= 12.3430 \text{ \AA}$ and $c=5.7840 \text{ \AA}$ [4].

L. Misoguti et. al. also reported the $P 2_1 2_1 2_1$ space group symmetry of the L-Alanine single crystals having unit cell sides $a= 6.0280 \text{ \AA}$, $b= 12.3450 \text{ \AA}$ and $c= 5.7850 \text{ \AA}$ possessing non-centrosymmetrical orthorhombic crystal structure [9].

P.Ilayabarathi et. al. prepared solution growth based semiorganic and non-linear optical crystals of L-Alanine cadmium bromide and reported its high degree of purity and crystallinity (using powder XRD analysis) along with findings of its orthorhombic crystal structure with its unit cell sides $a= 5.7710 \text{ \AA}$, $b= 6.0140 \text{ \AA}$ and $c=12.2980 \text{ \AA}$ obtained using Nonius CAD4 single crystal diffractometer [6].

P. Kalaiselvi et. al. reported the powder XRD analysis of solution grown L-Alanine cadmium chloride single crystals using Ricco Aulcima Model 3 confirming its monoclinic type of lattice structure with unit cell sides $a= 16.330 \text{ \AA}$, $b= 7.310 \text{ \AA}$ and $c=8.00 \text{ \AA}$ crystallizing within C_2 symmetry space group [7].

XRD analysis of L-Alanine L-Alaninium picricrate monohydrate crystals reported by S. Muhammad et. al. using both Single crystal as well as powder X-ray diffractometer shows the monoclinic type of crystal lattice of LALAP with unit cell lattice parameters (obtained from single crystal diffractometer) $a= 8.268 \text{ \AA}$, $b= 7.510 \text{ \AA}$ and $c=15.540 \text{ \AA}$ having $P2_1$ symmetry space group. Thereafter, the PXRD raw data was

inputted in CHECKCELL and POWDERX and a good agreement was reported between the crystal lattice parameters including sides, angles, space grouping and lattice type as obtained theoretically and experimentally [8].

M. Shkir et. al. reported his study in which he prepared solution grown HCl added L-Alanine crystals using slow evaporation technique. XRD analysis of the crystals obtained confirms its orthorhombic $P2_12_12_1$ space group symmetry revealing its non-centro-symmetric nature a necessitate condition to be used in NLO based device applications. Lattice parameters were calculated using POWDERX software giving values $a= 6.03588 \text{ \AA}$, $b= 12.3508 \text{ \AA}$ and $c=5.78641 \text{ \AA}$ [9].

N. Suresh et. al. reported the single crystal XRD analysis of pure form of LA as BNLA (Bismuth nitrate doped L-Alanine) showing orthorhombic structure in $P 2_12_12_1$ space group symmetry for both pure and doped form of LA. Volume expansion of unit cell was noted in BNLA due to slight shifting in the values of cell parameters without any change reported in its basic crystal structure [10].

T. Vela et. al. investigated the comparison between the crystal structure of pure LA and lithium sulphate added LA using XRD technique both in their single crystal and powdered form showing $P 2_12_12_1$ space group symmetric orthorhombic type of crystal structure having lattice parameters of values $a= 6.032 \text{ \AA}$, $b= 12.343 \text{ \AA}$ and $c=5.7841 \text{ \AA}$ (for LA) and $a = 5.782 \text{ \AA}$, $b= 6.008 \text{ \AA}$ and $c=12.295 \text{ \AA}$ (for LSLA) obtained using X-ray diffractometer in single crystal form and no change was reported in its basic structure due to admixturing of lithium sulphate [11].

A. Aravindan et. al. reported a change in the space symmetry and crystal structure of LA on reacting with nitric acid. Single crystal XRD analysis of pure LA crystal noted its orthorhombic crystal lattice type in $P 2_12_12_1$ space group with unit cell sides $a = 6.0320 \text{ \AA}$, $b= 12.3430 \text{ \AA}$ and $c=5.7840 \text{ \AA}$ (for LA) while L-Alanine alaninium nitrate crystallizes in the $P 2_1$ space group of monoclinic lattice type alongwith unit cell sides $a = 7.734 \text{ \AA}$, $b= 5.388 \text{ \AA}$ and $c=12.976 \text{ \AA}$ with enhanced NLO efficiency due to protonation of amino group (NH_3^+) [1]. A comparison for crystal structure, unit cell parameters and space group symmetry for above reported pure and doped LA single crystals is tabulated in table 2.

Table 2 for comparison of XRD properties

S. No.	Crystal prepared	Cell parameters of the crystal	Volume of Unit Cell	Lattice structure	Space group symmetry	Author
1	L-Alanine	$a = 6.0220 \text{ \AA}$ $b = 12.3230 \text{ \AA}$ $c = 5.7790 \text{ \AA}$	$V = 428.9 \text{ \AA}^3$	Orthorhombic	$P2_12_12_1$	M.L. Caroline et. al.
2	L-Alanine	$a = 6.032 \text{ \AA}$ $b = 12.343 \text{ \AA}$ $c = 5.784 \text{ \AA}$	----	Orthorhombic	----	N. Vijayan et. al.
3	Lithium Sulphate admixture L-	$a = 5.782 \text{ \AA}$ $b = 6.008 \text{ \AA}$	$V = 427.2 \text{ \AA}^3$	Orthorhombic	$P2_12_12_1$	T. Vela et. al.

	Alanine (LSLA)	c = 12.295Å				
4	L-Alanine	a = 5.773Å b = 6.008Å c = 12.346Å	V = 428.1Å ³	Orthorhombic	P ₂ ₁ 2 ₁	T. Thilak et.al.[12]
5	Bismuth nitrate doped LA crystals	a = 6.018Å b = 12.362Å c = 5.786Å	V = 430.44Å ³	Orthorhombic	P ₂ ₁ 2 ₁	N. Suresh et. al.
6	HCl added LA	a = 6.0350Å b = 12.350Å c = 5.7860Å	V= 431.36Å ³	Orthorhombic	P ₂ ₁ 2 ₁	M. Shkir et. al.
7	LALAPM	a = 8.2680Å b = 7.510Å c = 15.540Å	V = 931.0Å ³	Monoclinic	P ₂ ₁	S. Muhammad et. al.
8	LA	a = 6.0280Å b = 12.3450Å c = 5.7850Å	----	Orthorhombic	P ₂ ₁ 2 ₁	L .Misoguti et. al.
9	Co ²⁺ doped L-Alanine	a = 6.032Å b = 12.245Å c = 5.831Å	V = 430.68Å ³	Orthorhombic	P ₂ ₁ 2 ₁	M.L. Caroline et. al.
10	L-Alanine Cadmium Chloride	a = 16.33Å b = 7.31Å c = 8.00Å	V = 854Å ³	Monoclinic	C ₂	P. Kalaiselvi et. al.
11	L-Alanine Cadmium Bromide	a = 5.771Å b = 6.014Å c = 12.298Å	V = 426.8Å ³	Orthorhombic	P ₂ ₁ 2 ₁	P. Ilayabarathi et. al.
12	L-Alanine L-alaninium nitrate	a = 7.7342Å b = 5.3876Å c =	----	Monoclinic	C ₂	A. Aravindan et. al.

		12.9765Å				
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FTIR study

FTIR analysis of L-Alanine investigated by M.L. Caroline et.al. concludes its zwitterionic structure in which NH_3^+ whose presence is confirmed from the IR bands observed at 3082, 1620 and 1519 cm^{-1} [2] behave like a donor of hydrogen bonds whereas COO^- is a strong hydrogen bond acceptor. Observation of strong peak at 1362 and 1236 cm^{-1} [2] confirms CH_2 twisting and wagging modes.

M.L. Caroline et.al. also investigated the effect of Co^{2+} doping in L-Alanine single crystals and its FTIR analysis revealed the shift in vibrational wave numbers due to incorporation of metal dopants without altering its zwitterionic structure [3].

N.Vijayan et. al. carried out the middle IR region (450-4000 cm^{-1}) Fourier transform spectral analysis of L-Alanine single crystals observing the sharp intensity peak due to asymmetrical stretching of NH_3^+ ions at 2112.44 cm^{-1} while a less intensity peak due to symmetrical stretching of NH_3^+ ions is observed at 1518.92 cm^{-1} [4].

FTIR spectral analysis in the wavelength range (400-4000 cm^{-1}) for understanding the molecular structure and chemical bonding in Cadmium bromide L-Alanine crystals confirm the functionality of amino group by presence of stretching frequency at 2987 cm^{-1} and that of carboxylic acid group by observation of intensity peak at 1589 cm^{-1} as reported by P.Ilayabarathi et. al. [6].

P. Kalaiselvi et. al. also confirmed the protonation of L-Alanine NH_2 group by COOH group as observed from absorption peaks during FTIR spectral analysis [7].

IR spectral analysis carried out by S. Muhammad et. al. also confirmed the presence of Zwitterionic L-Alanine and L-Alaninium moieties causing characteristic vibrations in the crystal [8].

FTIR study carried out by T. Vela et. al. for identification of functional groups in L-Alanine and Lithium Sulphate added L-Alanine reveals the shift in the values of absorption peaks for different functional groups in LSLA as well as the presence of additional functional groups of NH and CH_2 observed with absorption peak values at 3387 and 2931 cm^{-1} respectively [11].

FTIR study conducted by A. Aravindan et. al. confirms the significant enhancement in the SHG efficiency of L-Alanine Alaninium nitrate over LA due to addition of nitro group in the LA molecule as observed by the shift in the absorption peak value seen in asymmetrical stretching from 2112.44 cm^{-1} (for LA) to lower wavenumber value of 1621.67 cm^{-1} (for LAAN) [1].

Dielectric study

Dielectric property of L-Alanine crystals is important to study as they can explore its dielectric behavior and is majorly attributed to describe its lattice dynamics. Low dielectric constant value of optical material need low pooling voltage and hence is able to resolve the problem of variation in the value of refractive index. Dielectric constant value for polished L-Alanine single crystals wherein both of its opposite sides are polished silver in order to establish electrical contact value can be calculated using the relation:

$$\epsilon_r = CL / \epsilon_0 A$$

Wherein C stands for capacitance, L is the crystal thickness, ϵ_0 is the dielectric constant of the sample in vacuum and A is its area of cross-section.

On the other hand, its dielectric loss can be measured using the below formula:

$$\epsilon'' = \epsilon_r D$$

Where D stands for dissipation factor.

Dielectric analysis of the single L-Alanine crystal conducted by M. L. Caroline et.al. [2] in the frequency range 50 Hz to 5 MHz confirms the decreasing trend of both dielectric constant and dielectric loss when the frequency is increased. At high frequencies, low value of dielectric loss depicts the enhanced optical quality and efficiency and hence is a very much suitable parameter in view of the second harmonic generation coefficient as described by Miller rule [13] (desirable in NLO for device applications) of L-Alanine single crystals.

Presence of ionic, electronic, space and dipolar polarization may be the possible cause for such a high value of dielectric constant in the low frequency regime [14].

In addition to above findings, P. Kalaiselvi et. al. also reported the decrease in the value of dielectric constant (ϵ_r) on continuously increasing its temperature from 40°C to 70°C and the low value of dielectric loss saturated at approximately 2 as observed from the power loss value of AC and DC voltages [7].

Increase in the value of dielectric constant with continuous increase in temperature from 35°C to 95°C as reported by T. Vela et.al. for pure LA and LSLA crystals may be attributed to crystal expansion and presence of crystal impurities and defects [11].

N. Suresh et. al. in his comparative dielectric investigation of pure LA and BNLA analyzed the presence of crystals defects/ impurities as the possible cause of reduced space charge polarization reducing the dielectric constant value in the lower frequency regime in BNLA as compared to LA crystals [10].

UV Vis NIR Spectroscopic study

This spectroscopic study of LA crystals and its doped form is generally employed to check the feasibility to be used in optical device applications. By knowing the absorption of UV and visible radiations causing excitation of π and σ orbital ground state electrons to higher energy states, atomic structure of the crystal can be explained [15]. M.L. Caroline et.al investigated the UV Vis study on the solution grown LA crystals in the wavelength range 200 -1200 nm and observed high degree of transmittivity in the ultra-violet region having lower cutoff value wavelength obtained at 240 nm and 245 nm for Co^{2+} ions doped LA single crystals and pure LA crystals respectively. Both the crystals were found to exhibit intense absorption band in the UV region because of the presence of aromatic ring as well as presence of C=O group [3].

UV Vis investigation done by N. Vijayan et. al. between 400 to 2000 nm wavelength range confirms the minimum absorption of pure LA crystals in visible region a prerequisite for NLO materials to be used in device applications [4].

L. Misoguti et. al. reported the absorption spectra of pure LA crystals at room temperature exhibiting good transparency between 2500 to 1600 nm wavelength range. COO^- and NH_3^+ ions are responsible for electronic transition occurring in the near UV region causing an increase in the absorption coefficient value [9].

UV Vis study reported by P.Ilayabarathi et. al. on L-Alanine cadmium bromide crystals reveals the transmittance nature of crystals in the entire visible region and transparency of crystals was found to be 85 % with the lower cutoff wavelength at 203 nm [5].

UV Vis spectroscopic comparative study of pure LA and L-Alanine Cadmium Chloride crystals investigated by P. Kalaiselvi et. al. confirms the enhancement in optical transmittance upon doping by

noting 100% transmittance of LACC crystals between 370nm and 410 nm. An increase in the bandgap value for LACC crystal (5.12 eV) was also observed as compared to pure LA crystal (4.75eV) [6].

M. Shkir et. al. reported the UV-Vis-NIR diffused reflectance spectroscopic study of HCl added LA crystals in which the value for indirect and direct bandgap was noted to be 5 eV and 5.64 eV respectively [10].

UV-Vis-NIR spectroscopic study investigated by N. Suresh et. al. for pure LA and bismuth nitrate doped LA crystals in the wavelength range 200-850 nm recording low absorbing capacity and high transmittance for both types of crystals within the range of 300-850 nm pointing out their suitability to be used in optical device applications. The direct and indirect band gap values estimated by Tauc's relation are 4.280 and 4.050 eV (for LA) and 5.450 and 5.160 eV (for BNLA) [11].

Bandgap value of 5.20 eV was reported for Lithium sulphate admixed LA crystals by T. Vela et. al. during its UV-Vis spectroscopic study in the wavelength range 200-1100 nm [8].

A comparative study of pure LA and L-Alanine alaninium nitrate (LAAN) crystals done by A. Aravindan et. al. confirms the shifting of absorption cutoff value from 240 nm (for pure LA) towards higher value of 467 nm (for LAAN) due to the presence of nitro group (NH₂) fundamental frequency overtones enhancing its suitability in optical device applications [1].

Second Harmonic generation efficiency

Generally Q switched Nd: YAG laser is used to test the Second Harmonic generation efficiency [2] property of LA and its doped form crystals. Second Harmonic generation conversion efficiency value for L-Alanine cadmium bromide crystal (9mV) was found to be approximately half of that of its reference material powdered KDP (19mV) as investigated by P.Ilayabarathi et. al. [5] while it was about 0.26 times of SHG efficiency value of powdered KDP in case of -Alanine cadmium chloride [6].

As per report of M.L. Caroline et.al. , SHG efficiency of pure LA crystals was noted 0.33 times to that of powdered KDP used as reference material [2].

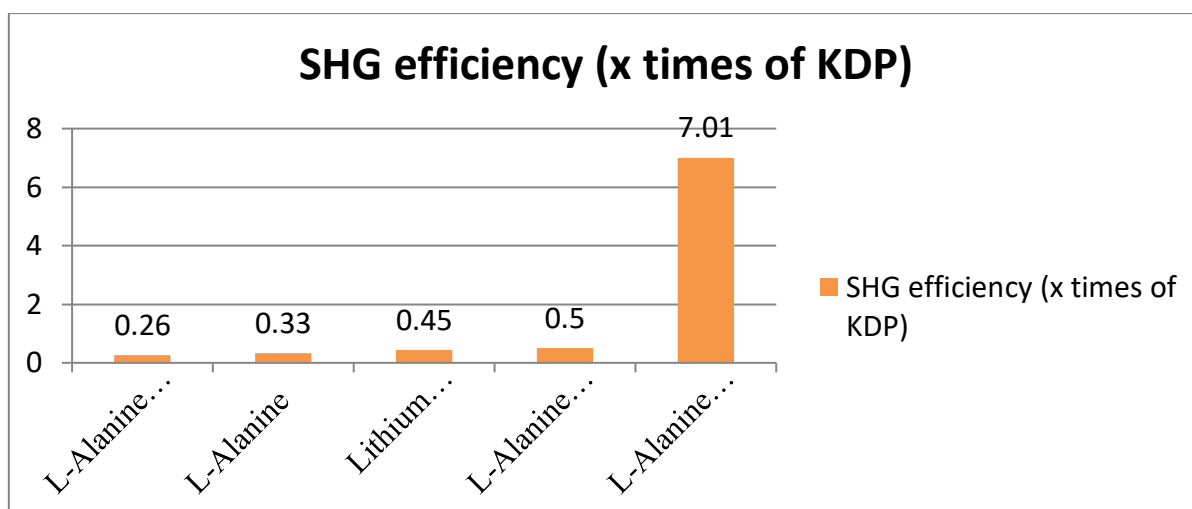
For LAAN crystals, SHG efficiency was 7.01 times higher as compared to reference powdered KDP material and 12.68 times greater than its pure form [1].

For Lithium sulphate admixed LA crystals SHG efficiency was 0.45 times that of reference powdered KDP material [8].

Below table 3 compare the SHG efficiency for above reported pure and doped LA single crystals.

Table 3 for Second Harmonic generation efficiency comparison

S. No.	Crystals prepared	Second Harmonic generation efficiency	Author
1	L-Alanine cadmium bromide	0.50 times that of KDP	P.Ilayabarathi et. al
2	L-Alanine cadmium chloride	0.26 times that of KDP	P. Kalaiselvi et. al.
3	L-Alanine	0.33 times that of KDP	M.L. Caroline et.al.
4	L-Alanine Alaninium nitrate	7.01 times that of KDP	A. Aravindan et. al.
5	Lithium sulphate admixed LA	0.45 times that of KDP	T. Vela et. al.



Graph 2 shows comparison of SHG efficiency of pure LA and its doped forms in comparison to KDP (Potassium di-hydrogen phosphate).

Comments on the formation of L-Alanine based compounds

Many comments have been proposed by different researchers claiming improper identification of L-Alanine based different compounds like L-Alanine L-Alaninium nitrate and L-Alanine cadmium bromide. B.R. Srinivasan et.al. in his paper put comments on the formation of L-Alanine cadmium bromide reporting it as L-Alanine itself because of the almost identical crystal structure as well as comparable unit cell parameters values among pure and doped forms of LA [16].

In his other paper, he also reported the comments on the erroneous investigation regarding formation of L-Alanine potassium nitrate and L-Alanine sodium nitrate both of which are infact L-Alanine itself as confirmed by him based upon the matching of PXRD peaks data of L-Alanine and so called LAPN and LASN without giving their justified chemical and structural formula as well as exact matching of IR data between pure and doped form of L-Alanine [17].

M. Fleck et.al. [18] also reported comments questioning novel formation of L-Alanine alaninium nitrate as reported by A. Aravindan et. al. [1] by comparing its unit cell parameters with the findings of M.R. Silva et. al. [19] during his dimeric formations of L-Alanine with Alaninium nitrate due to hydrogen bonding of L-Alanine with L-Alaninium cation wherein a good agreement in the values of unit cell parameters were observed but on the other hand intramolecular hydrogen bonding in the crystal structure of LAAN crystals structure as reported by A. Aravindan et. al. was in contradiction with the findings of M.R. Silva et. al..

Conclusion

It is concluded from the review of solution grown transparent single crystals of L-Alanine and its doped forms that in its pure form, L-Alanine crystallizes in noncentrosymmetric orthorhombic form having $P2_12_12_1$ type space group symmetry as confirmed from XRD analysis.

Doping of LA with nitric acid, picric acid and cadmium chloride causes change in its crystal structure to monoclinic having C_2 type space group symmetry alongwith increase in the value of unit cell parameters while doping with Lithium sulphate, bismuth nitrate, HCl, cadmium bromide and Co^{2+} left the crystal structure unchanged. Only increase in the values of unit cell parameters is observed confirming incorporation of doped material in the crystal structure of pure L-Alanine.

FTIR Spectral studies for pure LA concludes the presence of amine and carboxylic functional groups while for its doped forms presence of other functional groups viz CH₂, CH (for Co²⁺ doped LA) in addition to NH₃⁺ and COO⁻ is also confirmed. Second harmonic generation tabulated data confirms the enhancement in efficiency except for cadmium chloride LA crystals making them potential candidates to be used in NLO applications. Comments on the formation of many of the L-Alanine based compounds by different authors as reported by M. Fleck et.al. (for LAAN) and B.R. Srinivasan et.al. (for cadmium bromide doped LA) in case of Our review concludes the possibility of non-formation of LA doped compounds just by dissolving the desired dopants with LA in the given aqueous solvent because of no chemical reaction between them which in turn may be due to insufficient reaction conditions or any other reason. This may cause the erroneous nomenclature of solution grown doped LA crystals being infact LA itself in its original form.

References:

1. A. Aravindan, P. Srinivasan, N. Vijayan, R. Gopalakrishann, P. Ramasamy, A comparative study on the growth and characterization of nonlinear optical amino acid crystals: L-Alanine (LA) and L-Alanine alaninium nitrate (LAAN): *Spectrochimica Acta Part A* 71 (2008) 297-304. [URL: https://doi.org/10.1016/j.saa.2007.12.023](https://doi.org/10.1016/j.saa.2007.12.023)
2. M. Lydia Caroline, R. Sankar, R.M. Indirani, S. Vasudevan, Growth, optical, thermal and dielectric studies of an amino acid organic nonlinear optical material: L-Alanine: *Materials Chemistry and Physics* 114 (2009) 490-494. [URL: https://doi.org/10.1016/j.matchemphys.2008.09.070](https://doi.org/10.1016/j.matchemphys.2008.09.070)
3. M. Lydia Caroline, G. Mani, S. Usha, Effect of Co²⁺ on the growth, optical properties and laser damage threshold of potential nonlinear optical L-Alanine single crystal: *Optik* 125 (2014) 5069-5074. [URL: https://doi.org/10.1016/j.ijleo.2014.06.055](https://doi.org/10.1016/j.ijleo.2014.06.055)
4. N.Vijayan, S. Rajasekaran, G. Bhagavannarayana, R. Ramesh Babu, G.Gopalakrishann, M.Palanichamy, P.Ramasamy, Growth and characterization of nonlinear optical amino acid single crystal L-Alanine: *Crystal Growth & Design* 6 (2006) 2441-2445. [URL: https://doi.org/10.1021/cg049594y](https://doi.org/10.1021/cg049594y)
5. P.Ilayabarathi, J. Chandrasekran, Growth and characterization of L-Alanine cadmium bromide a semiorganic nonlinear crystals: *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 96 (2012) 684-689. [URL: https://doi.org/10.1016/j.saa.2012.07.027](https://doi.org/10.1016/j.saa.2012.07.027)
6. P. Kalaisevi, S. Alfred Cecil Raj, N.Vijayan, Linear and nonlinear optical properties of semiorganic single crystal: L-Alanine Cadmium chloride (LACC): *Optik* 124 (2013) 6978-6982. [URL: https://doi.org/10.1016/j.ijleo.2013.05.183](https://doi.org/10.1016/j.ijleo.2013.05.183)
7. Shabbir Muhammad, Mohd. Shkir, S. Alfaify, Ahmad Irfan, Abdullah G.Alsehemi, Combined experimental and computational insights into the key features of L-Alanine alaninium picrate monohydrate: growth, structural, electronic and nonlinear optical properties: *RSC Advances*, 5 (2015) 53988. [URL: https://doi.org/10.1039/C5RA05533D](https://doi.org/10.1039/C5RA05533D)
8. T. Vela, P. Selvarajan, T.H. Freeda, K. Balasubramanian, Growth and characterization of pure and semiorganic nonlinear optical Lithium Sulphate admixture L-Alanine crystal: *Physica Scripta*, 87 (2013) 045801. [URL: http://dx.doi.org/10.1088/0031-8949/87/04/045801](http://dx.doi.org/10.1088/0031-8949/87/04/045801)
9. L. Misoguti, A. T. Varela, F.D. Nunes, V.S. Bagnato, F.E.A.Melo, J. Mendes Filho, S.C. Zilio, Optical properties of L-Alanine organic crystals: *Optical Materials*, 6 (1996) 147-152. [URL: https://doi.org/10.1016/0925-3467\(96\)00032-8](https://doi.org/10.1016/0925-3467(96)00032-8)

10. Mohd. Shkir, I.S. Yahia, A.M.A. Al-Qahtani, Bulk monocrystal growth, optical, dielectric, third order nonlinear, thermal and mechanical studies on HCl added L-Alanine: L-Alanine organic NLO material: *Materials Chemistry and Physics*, 184 (2016) 12-22. [URL: https://doi.org/10.1016/j.matchemphys.2016.07.052](https://doi.org/10.1016/j.matchemphys.2016.07.052)
11. N. Suresh, M. Selvapandiyan, Faruq Mohamamad, Suresh Sagadevan, Influence of bismuth nitrate doping towards the characteristics of L-Alanine nonlinear optical crystals: *Chinese Journal of Physics*, 67 (2020) 349-359. [URL: https://doi.org/10.1016/j.cjph.2020.07.014](https://doi.org/10.1016/j.cjph.2020.07.014)
12. T. Thilak, M. Basheer Ahamad, G. Marudhu, G. Vinitha, Effect of KDP on the growth, thermal and optical properties of L-Alanine single crystals: *Arabian Journal of Chemistry*, 5 (2013)286. [URL: https://doi.org/10.1016/j.arabjc.2013.04.022](https://doi.org/10.1016/j.arabjc.2013.04.022)
13. C. Justin Raj, S. Dinakaran, S. Krishann, B. Milton Boaz, R. Robert, S. Jerome Das, Studies on optical, mechanical and transport properties of NLO active L-alanine formate single crystal grown by modified Sankaranarayanan-Ramasamy (SR) method:*Optics Communications*, 281 (2008) 2285-2290. [URL: https://doi.org/10.1016/j.optcom.2007.12.019](https://doi.org/10.1016/j.optcom.2007.12.019)
14. M. Vimalan, T. Rajesh Kumar, S. Tamilselvan, P. Sagayaraj, C.K. Mahadevan, Growth and properties of novel organic nonlinear optical crystal: L-alaninium tartrate (LAT) *Physica B: Condensed Matter*, 405 (2010) 3907-3913. [URL: https://doi.org/10.1016/j.physb.2010.06.026](https://doi.org/10.1016/j.physb.2010.06.026)
15. A. Ashour, N. El-Kadry, S.A. Mohmoud, On the electrical and optical properties of CdS films thermally deposited by a modified source, *Thin Solid Films* 269 (1995) 117–120. [URL: https://doi.org/10.1016/0040-6090\(95\)06868-6](https://doi.org/10.1016/0040-6090(95)06868-6)
16. B.R. Srinivasan, On the existence of ‘L-Alanine cadmium bromide’: *Spectrochimica Acta part A: Molecular and Biomolecular spectroscopy* 116 (2013) 639-641. [URL: https://doi.org/10.1016/j.saa.2013.07.052](https://doi.org/10.1016/j.saa.2013.07.052)
17. B.R. Srinivasan, A.M.Petrosyan, Infact L-Alanine: *Journal of Crystal Growth*, 533 (2020) 125477. [URL: https://doi.org/10.1016/j.jcrysgro.2019.125477](https://doi.org/10.1016/j.jcrysgro.2019.125477)
18. M. Fleck, A.M. Petrosyan, Comments on papers reporting IR spectra and other data of alleged L-Alanine alaninium nitrate and L-Alanine sodium nitrate crystals: *Crystal Research & Technology*, 44 (2009) 769-772. [URL: https://doi.org/10.1002/crat.200900150](https://doi.org/10.1002/crat.200900150)
19. M. R. Silva, J. A. Paixao, A. M. Beja, and L. A. da Veiga, Strong hydrogen-bonded amino acid dimmers in L-Alanine alaninium nitrate: *Acta Crystallographica C* 57 (2001) 838-840. [URL: https://doi.org/10.1107/S0108270101006072](https://doi.org/10.1107/S0108270101006072)