Crystal Growth and Characterization of Magnesium-Doped LAHC Single Crystals

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ABSTRACT

Single crystals of Mg doped L Alanine Hydrogen chloride (Mg doped LAHC) have been synthesized. The synthesized material has been purified by repeated recrystallization process. Single crystals were grown by slow evaporation method. The spectroscopic techniques namely, Fourier Transform InfraRed (FTIR), UV-VIS-NIR were used to study the properties of the crystals. The structural and lattice parameters determination was done by X-ray diffraction. The thermal stability studies were carried out. The thermoanalytical parameters like activation energy, entropy for activation and Arrhenius pre exponential factor needed for a chemical reaction were found using Coats- Redfern method.

KEYWORDS: Mg doped LAHC, FTIR, TGA, Activation Energy, Entropy, Coats- Redfern.

INTRODUCTION

In recent years, organic – inorganic hybrid materials have attracted considerable attention. Nonlinear optical (NLO) materials play vital role in various fields of science and technological developments [1,2,3]. They have gathered much attention for their high non-linear coefficient, high-laser damage threshold and high optical non-linearity [4,5,6]. Also they are useful in optical information processing, optical communication and data storage [7]. Organic NLO materials have poor mechanical and thermal properties resulting in the damage of the crystal during processing studies. Recently this drawback has been overcome by forming semi-organic NLO crystals. The combinations of organic-inorganic compounds bring the advantages such as high resistance to optical damage, multifaceted application and enhancement in the mechanical and thermal properties of the crystals etc. Researchers prefer amino acid based crystals since they are potential candidates for optical second harmonic generation (SHG) [8,9]. Hence they are used in many electronic and optoelectronics devices.

L-alanine is a promising amino acid and several semi organic NLO crystals such as L-alanine single crystals, L-alanine tartarate, L-alanine maleate [10,11,12] have been reported. In the present work, Magnesium doped L-alanine hydrogen chloride single crystals (Mg doped LAHC), a semi organic non-linear optical material has been synthesized and a systematic study has been carried out. An attempt has been made to study the effect of Magnesium chloride dopant on the physico- chemical properties of LAHC. The lattices parameters of the crystal were determined by the Single Crystal X-ray diffraction. The powder X-ray diffraction studies were done. The functional groups present in this crystal were confirmed by the FTIR spectroscopic technique. The grown doped crystals were studied using FTIR spectroscopic techniques in the range 400-4000 cm^{-1}. The vibrational band assignments were carried out for the crystal. UV-Vis NIR studies have been carried out for crystal. The variation of mass with the temperature was studied using the TGA and DTA. Inductively coupled plasma analysis has been used to confirm the presence of dopant in the crystal.

MATERIALS AND METHODS

Crystal growth

Analytical grade (AR grade) of L-alanine and concentrated hydrochloric acid were taken in the ratio 1:0.5 normality. Doubly deionized water was used as the solvent. Single crystals of pure LAHC were grown from supersaturated solution at room temperature by slow evaporation method.

$C_3H_7NO_2 + HCl \rightarrow C_3H_8NO_2^+Cl^-$

The dopant Magnesium chloride was added separately with the pure LAHC solution, in definite molecular ratio LAHC:X (X is dopant) being 1:0.01 in molar weight. Good quality doped crystals were obtained in the period of two weeks. The dimensions of them are in the range 13mm x 6mm x 8mm. All the grown crystals were colorless, stable and transparent. The quality of single crystals obtained was enhanced by successive recrystallization. The Photograph of as grown Mg doped LAHC crystals is presented in Figure.1

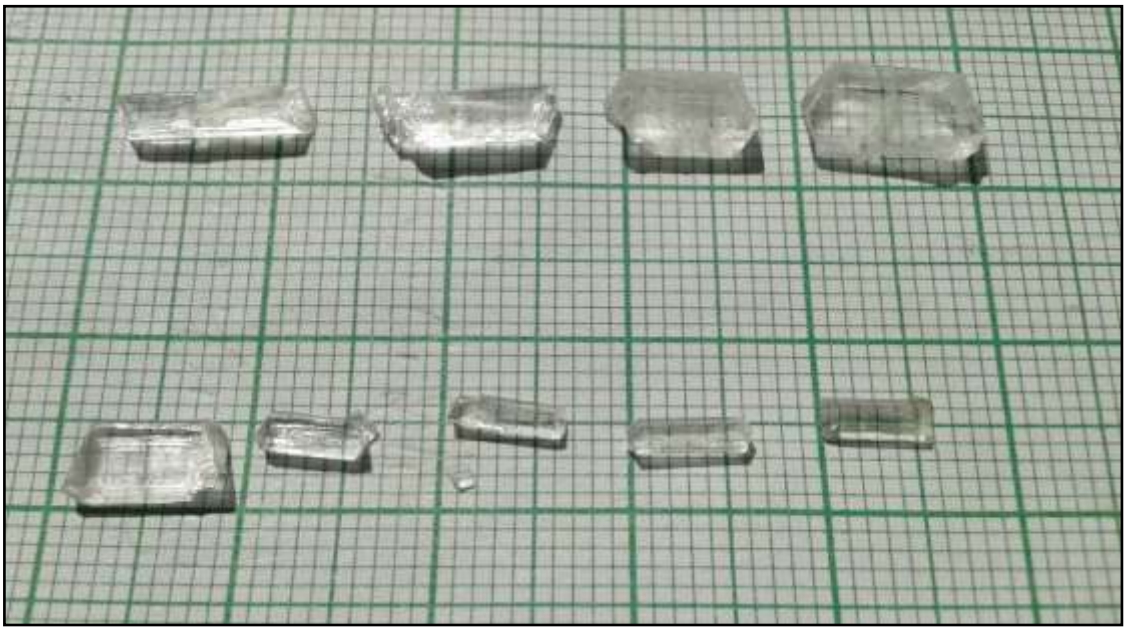

Figure 1: Photograph of Mg doped LAHC crystal

RESULTS AND DISCUSSION

Single Crystal XRD studies

The grown crystals of Mg doped LAHC were subjected to single crystal X-ray diffraction studies using ENRAF NONIUS CAD4 diffractometer with MoKα radiation (λ=0.71073 Å) to determine the crystal structure. The measurement was carried out at SAIF, IIT Madras, Chennai. The obtained values of cell parameters of LAHC crystal in this work are found to be in close agreement with the data reported in literature [13]. The single crystal XRD data for Mg doped LAHC are provided in the Table 1. The structure of the crystal is confirmed to be orthorhombic and the number of molecules per unit cell is 4. The space group of Mg doped LAHC crystal is $P2_12_12_1$and this space is recognized as non-centrosymmetric. It is the essential requirement for SHG from the sample. Figure 2 and 3 represent the XRD image of Mg doped LAHC and structure of crystal respectively.

Table 1: Single Crystal XRD data of Mg doped LAHC

Diffractometer	ENRAF NONIUS CAD-4
Radiation, wavelength	MoKα, 0.71069 Å
Symmetry	Orthorhombic structure
Space group	$P2_12_12_1$.
Lattice constants	a= 5.80 Å b=6.04 Å c=12.38 Å α=90° β=90° γ =90°
Volume	434 $Å^3$

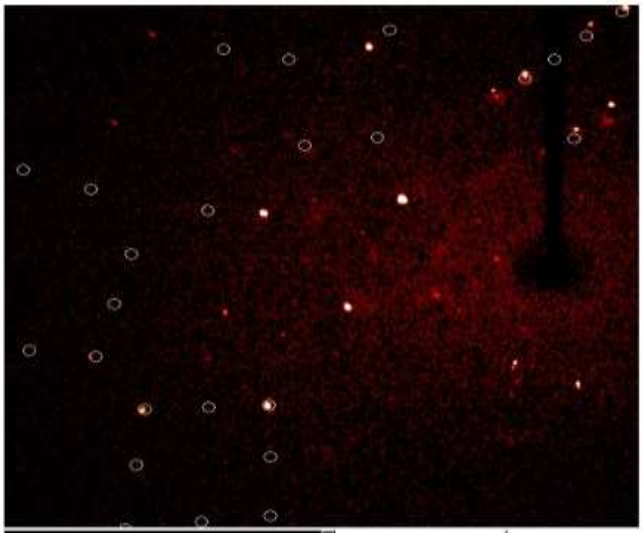

Figure 2: XRD image of Mg doped LAHC

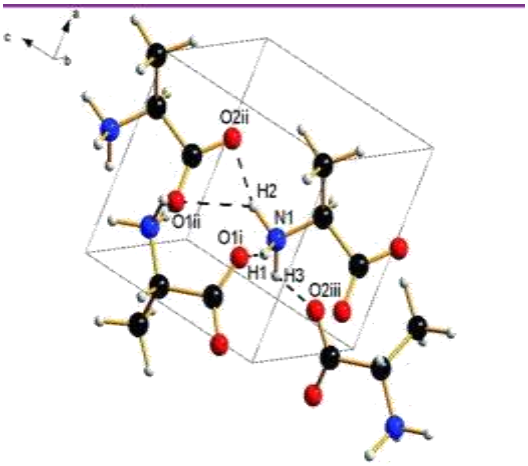

Figure 3: structure of crystal.

Powder XRD Studies

The fine power of as grown Mg doped LAHC crystal has been subjected to powder X-ray diffraction analysis and the recorded pattern is shown in Figure 4. The measurement was carried out at Material Science Group (MSG), IGCAR, Kalpakkam. The powder sample was scanned in steps of 0.1° for a time interval of 10 seconds over a 2Θ range of 10° to 60°.The sharp and well defined Bragg's peaks at specified 2Θ angles show the crystalline nature and purity of the crystal.

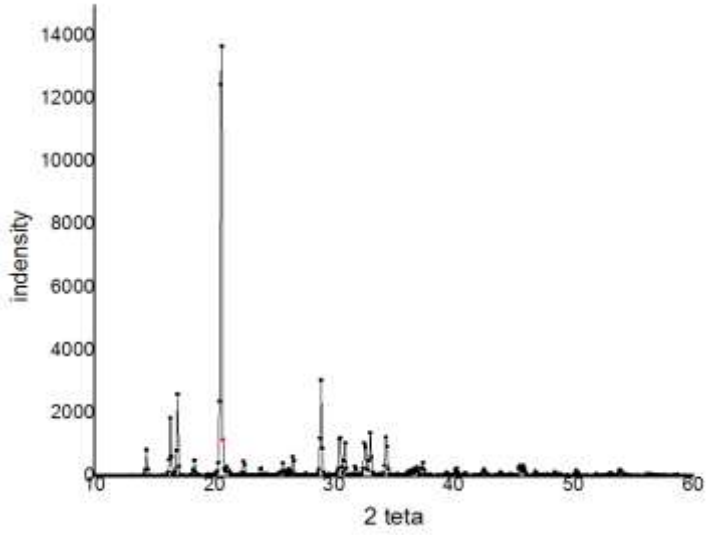

Figure 4: powder XRD pattern of Mg doped LAHC crystal

FT-IR Analysis

The FT-IR spectrum of Mg doped LAHC crystal was recorded in the region 4000-400 cm^{-1} using Perkin Elmer FTIR Spectrometer at SAIF, IIT madras, Chennai. The sample was prepared by pressing Mg doped LAHC with KBr into pellet form. The observed spectrum is shown in Figure 5.

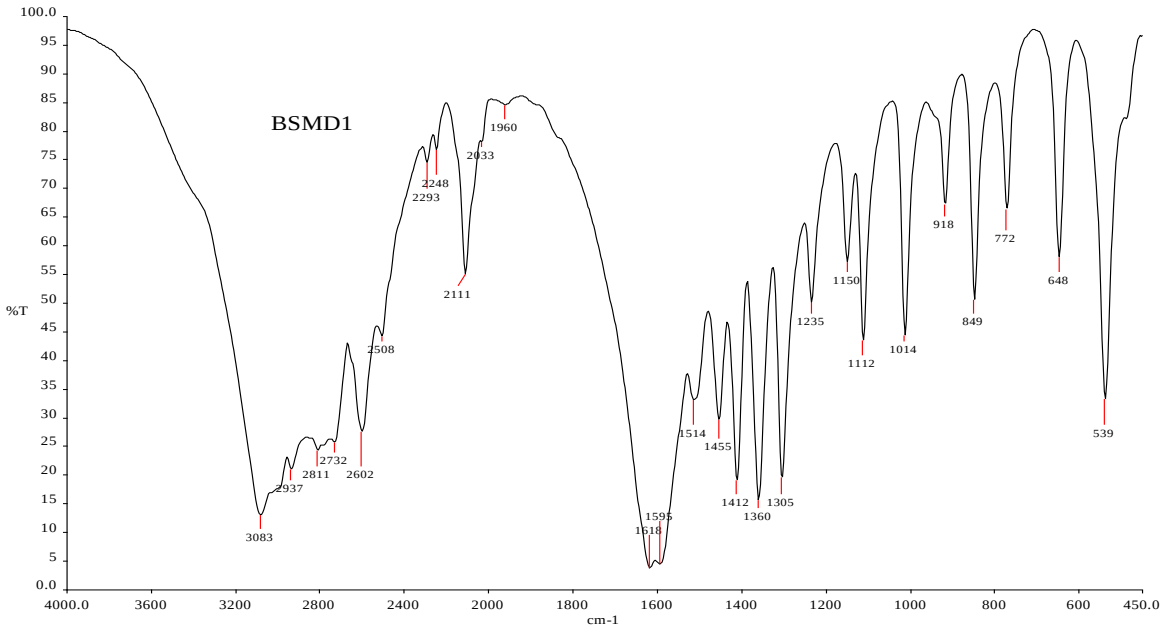

Figure 5: FTIR spectrum of Mg doped LAHC

The absorption peaks at 3083, 1618, 1514 cm^{-1} show the presence of NH_3^+ group in the crystal. The peaks at 2811, 2732, 2508, cm^{-1} are attributed to the C-H stretching mode vibrations. The peaks at 1412, 1306, 1235 and 1112 cm^{-1} are due to COO^- symmetric stretching mode. The absorption peak at 2111 cm^{-1} is due to the combination band of NH_3^+ degenerate mode and NH_3^+ torsion. The peak at 1618 cm^{-1} is due to the deformation of NH_3^+. The peak at 1514 $cm^{-1}$of weak intensity belongs to symmetric NH_3^+ deformation. The O-C-O bending mode at 772 cm^{-1} has been identified and assigned. The COO^- scissoring mode appears at 648 cm^{-1} in the FT-IR spectrum of the crystal. The peak at 539 cm^{-1} represents the COO^- rocking. The vibrational band assignments for the absorption peaks of the FT-IR spectrum have been done in accordance with the data reported in the literature [14-17].

Table 2: The vibrational band assignments of Mg doped LAHC

Frequency cm^{-1}	Band assignment
3083(vs)	NH_3^+ stretching
2811(s)	C-H stretching
2732(s)	C-H stretching
2508(m)	C-H stretching
2111(m)	NH_3^+ degenerate mode and NH_3^+ torsion
1618(vs)	Asymmetric deformation of NH_3^+
1514(s)	Symmetric deformation of NH_3^+
1412(vs)	COO^- symmetric stretching
1306(s)	COO^- symmetric stretching
1235(s)	COO^- symmetric stretching
1112(m)	COO^- symmetric stretching
772(w)	COO^- scissoring
539(m)	COO^- rocking

vs -very strong, m-medium, w- weak, s- strong

Optical Transmission studies

The optical properties of the grown crystals were studied using Perkin Elmer Lambda 35V, UV-Vis NIR spectrophotometer in the wavelength 200-1100 nm at Material Science Group (MSG), IGCAR Kalpakkam. The UV-Vis NIR absorption and transmittance spectra of doped LAHC crystals are shown in figure 6.

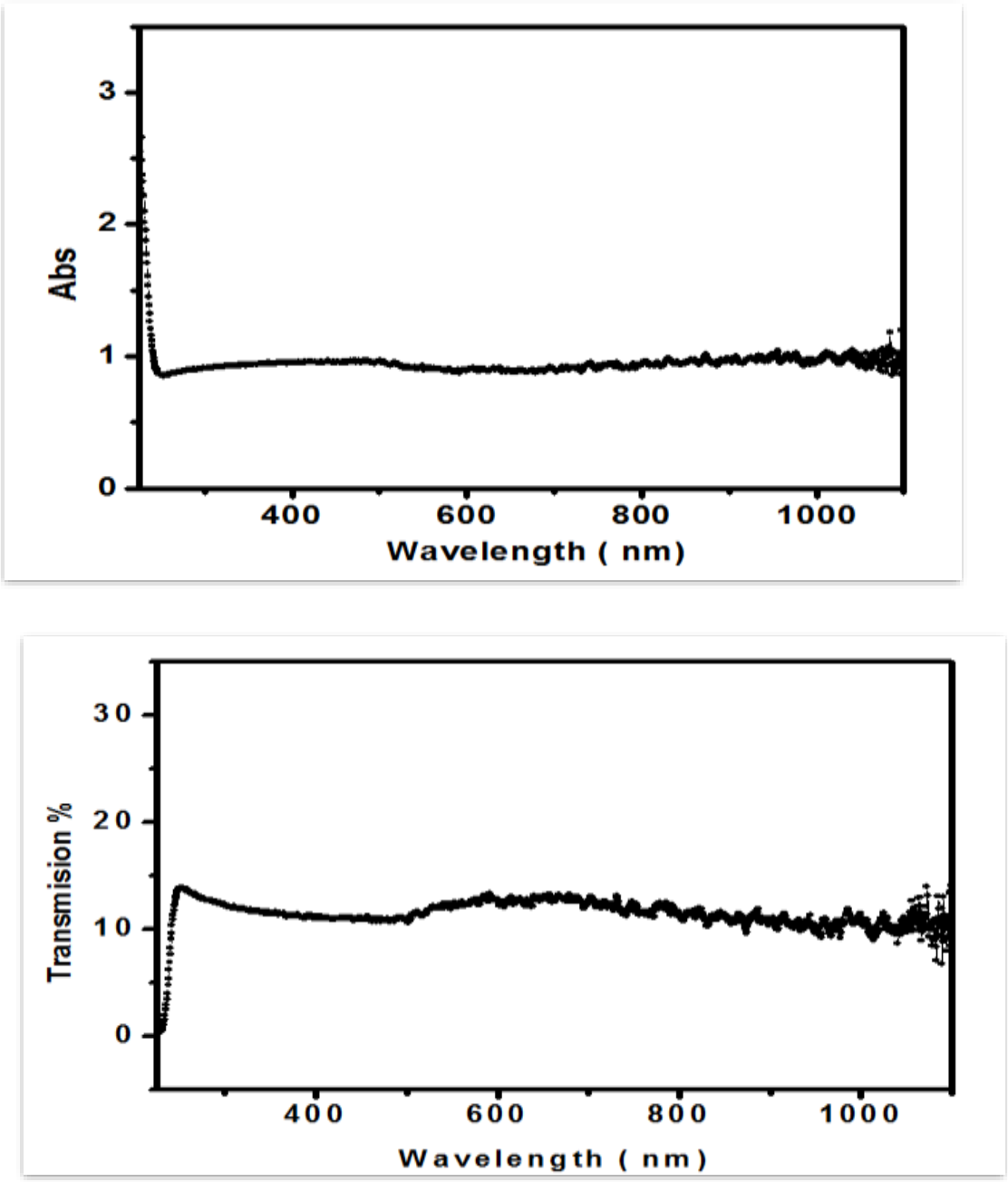

Figure 6: UV absorption & transmission graph of the Mg doped LAHC

This spectral study is helpful 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 the electronic structure. This reveals the band structure of the crystal and to know if the crystal gets affected in the band extreme or not.

From the spectra presented in figure 6, it is clear that Mg doped LAHC crystals have transmittance in the entire of visible –NIR region of the spectra. High transmission in the entire visible region and short cut off wavelength facilitates the as grown crystals of the present work to be potential candidates for nonlinear optical materials producing second harmonic and third harmonic of Nd:YAG laser. However, absorption at around 251 nm occur in the near ultraviolet region in the crystal arises due to electronic transitions associated within the sample. The cut off wavelength (λ) is around 251 nm. Using the formula E_g=hc/ λ, the band gap energy was found to be 4.9314 eV.

ICP-OES studies

Inductively Coupled Plasma (ICP) technique has been used to detect the presence of dopant in the crystal. Perkin Elmer Optima 5300 DV at SAIF IIT Madras, Chennai was used for the study.

The primary goal of the Inductively Coupled Plasma studies is to get the elements to emit characteristic wavelength specific light, which can then be measured. The presence of magnesium in the doped MgLAHC crystal is confirmed by the ICP- optical emission spectrometry studies. Magnesium is identified with the wavelength 285.213nm in the ICP study. The presence of Magnesium is confirmed by comparing the emitted wavelength with the characteristic wavelength for Mg (285.2 nm) in the ICP-OES standard measurements. (Table 3)

Table 3: ICP test data of Mg doped LAHC

Sample weight	Analyte	Concentration
0.125	Mg 285.213	0.219 mg/L

The weight percentage of Magnesium present in the doped crystal can be calculated from the formula,

$$\text{Weight \%} = \frac{\text{ppm (mg/l)} \times \text{volume in ml} \times 10^{-4}\text{(dilution factor)}}{\text{Weight of the sample (g)}}$$

Weight % = 0.1752%

From the ICP spectrometry, it is evident that Magnesium is present in the Mg doped LAHC crystal.

Thermal Analysis

Thermal gravimetric (TG) and Differential Thermal Analysis (DTA) of Mg doped LAHC crystal were carried out between 20°C and 1400ºC in Nitrogen atmosphere at a heating rate of 20ºC/min using Q500V20.10 Thermal analyser at SAIF, IIT Madras, Chennai. The TGA and DTA curves of the crystal are shown in figure 7 and figure 8 respectively. From the TGA curve, it is clear that the crystal is stable till 295.0 ºC. The endothermic peak at 297.6ºC shows 96.84% decomposition of LAHC crystal.

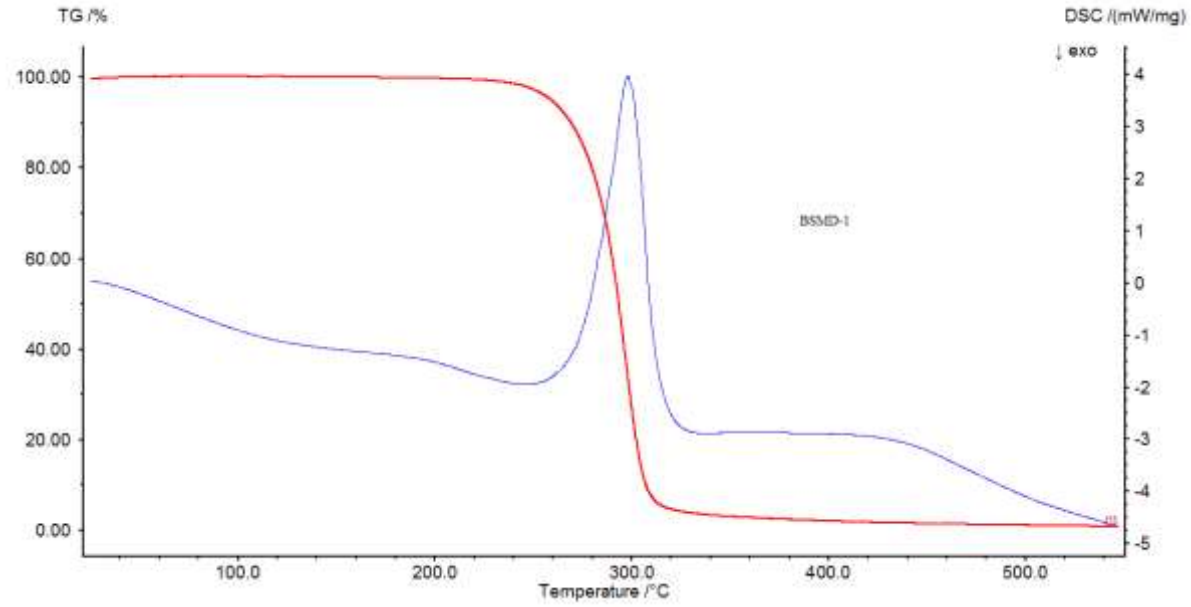

Figure 7 :Thermogram of Mg doped LAHC Crystal

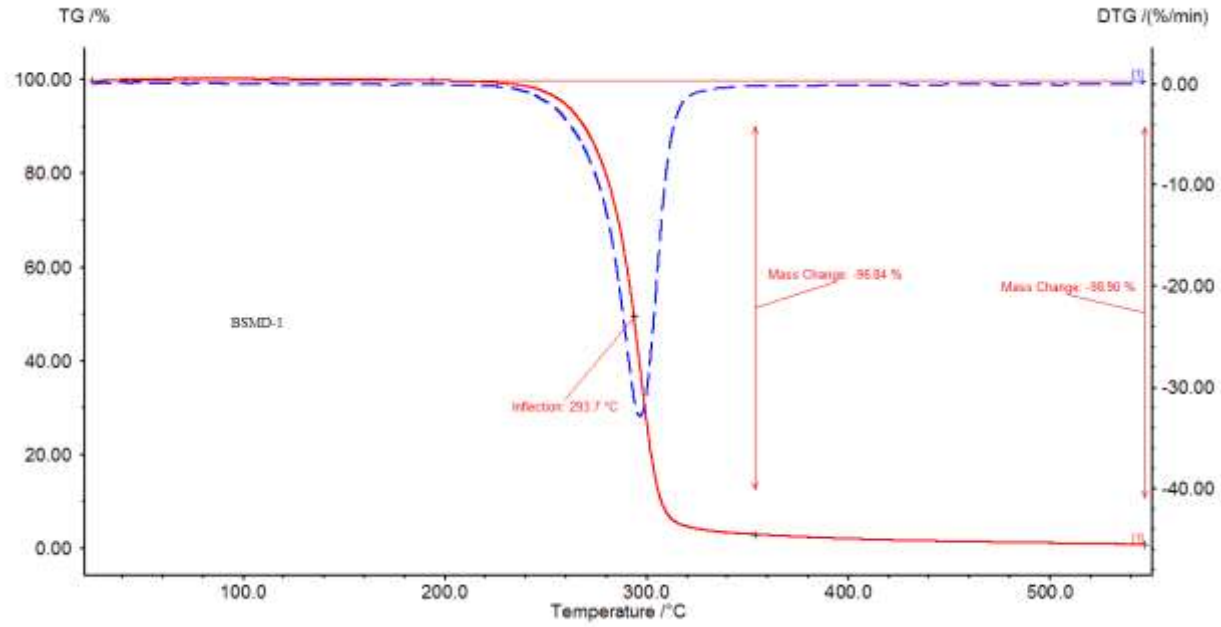

Figure 8 Differential Thermal Analysis of Mg doped LAHC Crystal

Theory of Coats-Redfern Method

Kinetic analysis of TG data of any dehydration/decomposition process by any method is usually based on the following two primary equations (i) and (ii).

$\frac{d\alpha}{dt} = Kf(\alpha)$ (i) and

$K = A \exp [-E/RT]$

$\ln K = \ln A - [E/RT]$ (ii)

Where, α is the fraction of the sample decomposed at a time t.

$\alpha = [(W_0 - W_t)/(W_0 - W_\infty)]$ (iii)

where, W is the weight of the solid (subscript 0 and ∞ refer to the initial and residual amount respectively). $\frac{d\alpha}{dt}$ is the rate of reaction and F(α) is the mathematical expression in α describing the kinetic and mechanical step. Many equations relating the rate of solid state reaction to α and the mathematical models for the reaction mechanisms have been applied to various systems. But sometimes, the decompositions following a particular mechanism have been found to shifting to another mechanism after some time in isothermal methods. However, many authors support the use of empirical kinetic laws of the type $f(\alpha) = (1-\alpha)^n$ where is the order of the reaction on the basis of these fundamental equations and their derivatives, many differential and integral method have been developed. Out of many methods the Coats – Redfern method has been used in present work for the approximation of kinetic parameters of dehydration/ first step decomposition of Mg doped LAHC single crystal. Attempts have also been made to find any pattern in the onset temperature of thermal dehydration and thermal decomposition for various inorganic compounds and transition metals. The present study claims its significance for being the first attempt in the thermo analytical studies of semi-organic NLO crystal, Mg doped LAHC.

For n = 1

$\log[-\log\{(1-\alpha)/T^2\}] = \log(AR/\beta E)[1-2RT/E] - E/2.303RT$ (iv)

In the above equation, left hand side is given as Y. This equation is similar to linear equation Y=MX+C.

Where

$Y = \log[-\log\{(1-\alpha)/T^2\}]$

$M = -E/2.3032R$

$C = \log(AR/\beta E)[1-2RT/E]$

$X = 1/T$

For $n \neq 1$

$\log(1-\{1-\alpha)^{1-n}\}\{1/T^2(1-n)\}] = \{\log_{10}(AR/\beta e)\}[1-2RT/E] - E/2.303RT$ (v)

Where n - is the order of reaction

By plotting the appropriate left hand side of the above equation (iv) versus 1/T, i.e.,

$\log_{10}[1-(1-\alpha)^{1-n}/T^2(1-n)]$ against 1/T For $n \neq 1$ (vi)

$\log_{10}[-\log_{10}(1-\alpha)/T^2)]$ against 1/T For n=1 (vii)

should result in a straight line of slope –E/2.303R for the correct value of n, since it may be shown that for most values of E and for the temperature range over which reactions generally occur the expression $\log_{10}AR/\beta E[1-(2RT/E)]$ is sensibly constant. The values of E, the activation energy of the reaction and A, the pre-exponential factor can be calculated from these equations.
The Entropy of activation is obtained using the thermodynamic relation

$$\Delta S = 2.303R \log (Ah/kT_{1/2}) \quad \text{(viii)}$$

Where h is the Planck's constant, k the Boltzmann constant and $T_{1/2}$ the temperature at which half of the transformation is complete. The entropy of activation ΔS has been found for Mg doped LAHC single crystal.

THERMO ANALYTICAL STUDIES

Activation energy is the minimum energy required to start the chemical reaction in kilojoule/mole. The higher the Activation Energy the slower the reaction. Coats-Redfern method has been used by researches to analyse non-isothermal conditions of thermoanalytical kinetics of the crystals For a chemical reaction to proceed at a reasonable rate, there should exist an appreciable number of molecules with energy equal to or greater than Activation energy. This is called Arrhenius Activation Energy, which tests the sensitivity of the reaction rate to the room temperature. The equations (i)-(viii) are solved for the TGA data of Mg doped LAHC with MS EXCEL software and the results are projected in Table 4.

Table 4 Activation Energy Analysis – Coats Redfern Method

TABLE FOR COATS-REDFERNS RELATION										
Temp(°c)	Temp(°k)	T^2(°K)	weight(%)	weight(mg)	weightloss(mg)	α	1-α	{-LOG(1-α)/T	LOG{-LOG(1-α)/T	1/T
255.2	528.2	278995.24	96.12833	8.120921318	0.327078682	0.039043892	0.960956108	6.20E-08	-7.207639861	0.001893222
257.7	530.7	281642.49	95.4336	8.062230528	0.385769472	0.046049903	0.953950097	7.27E-08	-7.138488192	0.001884304
260.2	533.2	284302.24	94.58875	7.9908576	0.4571424	0.0545698	0.9454302	8.57E-08	-7.066915321	0.001875469
262.7	535.7	286974.49	93.54998	7.90310231	0.54489769	0.065045286	0.934954714	1.02E-07	-6.992320295	0.001866716
265.2	538.2	289659.24	92.30388	7.797831782	0.650168218	0.077611593	0.922388407	1.21E-07	-6.916751497	0.001858045
267.7	540.7	292356.49	90.89696	7.678975181	0.769024819	0.091799691	0.908200309	1.43E-07	-6.8445458	0.001849454
270.2	543.2	295066.24	89.28371	7.542687821	0.905312179	0.108068525	0.891931475	1.68E-07	-6.773838389	0.001840943
272.7	545.7	297788.49	87.32252	7.37700649	1.07099351	0.127846164	0.872153836	1.99E-07	-6.700070984	0.001832509
275.2	548.2	300523.24	85.07862	7.187441818	1.260558182	0.150474794	0.849525206	2.36E-07	-6.627699263	0.001824152
277.7	550.7	303270.49	82.49524	6.969197875	1.478802125	0.176526913	0.823473087	2.78E-07	-6.555742028	0.001815871
280.2	553.2	306030.24	79.44918	6.711866726	1.736133274	0.207244933	0.792755067	3.30E-07	-6.482041187	0.001807664
282.7	555.7	308802.49	75.85256	6.408024269	2.039975731	0.243515081	0.756484919	3.92E-07	-6.406179158	0.001799532
285.2	558.2	311587.24	71.53178	6.043004774	2.404995226	0.287088026	0.712911974	4.72E-07	-6.326368431	0.001791473
287.7	560.7	314384.49	66.40881	5.610216269	2.837783731	0.338750664	0.661249336	5.71E-07	-6.243070755	0.001783485
290.2	563.2	317194.24	60.0381	5.072018688	3.375981312	0.402996148	0.597003852	7.06E-07	-6.151032942	0.001775568
292.7	565.7	320016.49	52.96538	4.474515302	3.973484698	0.474321058	0.525678942	8.73E-07	-6.059133424	0.001767721
295.2	568.2	322851.24	44.19481	3.733577549	4.714422451	0.562767952	0.437232048	1.11E-06	-5.953559731	0.001759944
297.7	570.7	325698.49	35.40731	2.991209549	5.456790451	0.651385576	0.348614424	1.41E-06	-5.852277868	0.001752234
300.2	573.2	328558.24	26.70199	2.255784115	6.192215885	0.739174456	0.260825544	1.78E-06	-5.750459965	0.001744592
302.7	575.7	331430.49	19.15198	1.61795927	6.83004073	0.815312601	0.184687399	2.21E-06	-5.654955198	0.001737016
305.2	578.2	334315.24	13.2285	1.11754368	7.33045632	0.87504799	0.12495201	2.70E-06	-5.568344958	0.001729505
307.7	580.7	337212.49	9.48167	0.801011482	7.646988518	0.912832931	0.087167069	3.14E-06	-5.502742211	0.00172206
310.2	583.2	340122.24	7.40782	0.625812634	7.822187366	0.933746691	0.066253309	3.47E-06	-5.460197695	0.001714678
312.7	585.7	343044.49	6.12331	0.517297229	7.930702771	0.946700343	0.053299657	3.71E-06	-5.430428035	0.001707359
315.2	588.2	345979.24	5.44674	0.460140595	7.987859405	0.95352322	0.04647678	3.85E-06	-5.414296798	0.001700102
317.7	590.7	348926.49	4.93383	0.416809958	8.031190042	0.958695665	0.041304335	3.97E-06	-5.40159648	0.001692907

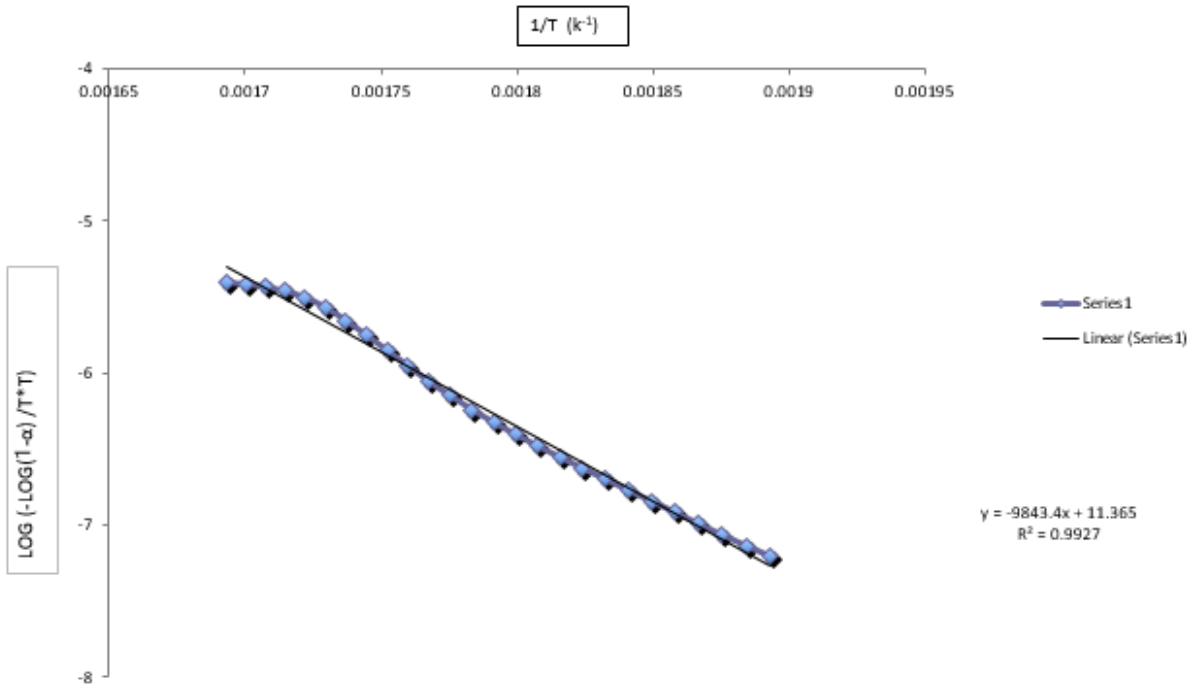

Figure 9: Graph LOG (-LOG(1-α) /T*T) vs 1/T

Table 5: Thermodynamical parameters of Mg doped LAHC

Thermodynamical parameter	**value**
Activation energy (E)	-188.48 kJ/ mole
Arrhenius pre exponential Factor (A)	11.365 S^{-1}
Entropy (S)	-11.69 J/K

Comparing the result from graph with equation (iv) from the slope the Activation energy (E) is found to be -188.48 kJ/ mole. The pre exponential factor / Arrhenius pre exponential (A) is found from the constant value (C) in equation (iv). The entropy is determined using equation (viii). The Table 5 presents various thermo dynamical parameters determined using Coats – Redfern Method.

CONCLUSION

A systematic study has been carried out on the growth of Magnesium chloride doped L-alanine hydrogen chloride crystals (Mg doped LAHC). The lattices parameters of the crystal were determined by the Single Crystal X-ray diffraction. The structure of the crystal was confirmed as orthorhombic. The powder X-ray diffraction studies revealed the crystalline nature of the sample. The functional groups present in this crystal were confirmed by the FTIR spectroscopic technique. The vibrational band assignments of the fingerprint region confirm the structure of the crystal. The optical transparency of the crystal studied using UV-VIS-NIR reveals that the grown crystal is a potential candidate for optoelectronics. Inductively coupled plasma analysis has been used to confirm the presence of dopant in the crystal. The variation of mass with the temperature studied using the TGA was used to find thermodynamical parameters such as activation energy, entropy etc. associated with the non-isothermal kinetic analysis.

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