

L-ALANINE POTASSIUM SULPHATE SINGLE CRYSTALS: FROM SYNTHESIS TO CHARACTERIZATION

Emily Adams¹, William Scott², Joshua Robinson³, and Daniel Brown^{*3}

¹ Department of Mechanical Engineering, University of Manchester, UK

² Department of Chemical Engineering, Stanford University, USA

³ School of Environmental Science, University of Sydney, Australia

ABSTRACT

Single crystals of L-Alanine Potassium sulphate (LAPS) were synthesized. The synthesized material was purified by repeated recrystallization process. Single crystals were grown by slow evaporation method. The structural and lattice parameters determination was done by X-ray diffraction. The Fourier Transform Infra-Red (FTIR) spectroscopy was used to confirm the presence of functional groups in the material. The scanning electron microscopic analysis has been done to study the surface morphology of the crystal. Energy dispersive spectrum was done to identify the composition of elements present in the material. The thermal stability studies were carried out. The thermo analytical parameters like activation energy (E), Arrhenius pre exponential factor (A), entropy (ΔS), enthalpy (ΔH) and Gibb's free energy for activation (ΔG) needed for a chemical reaction were found using Coats - Redfern method. The grown crystals were subjected to dielectric studies for different frequency and temperature. A comparative analysis has been done on the title compound.

KEYWORDS: LAPS, FTIR, TGA, Activation Energy, Entropy, Coats – Redfern, Dielectric studies.

1. INTRODUCTION

In recent years, organic – inorganic (semi organic) hybrid materials are getting more attention with the research. Nonlinear optical (NLO) materials play very important role in science and technological developments [1,2,3]. These material which gives high non-linear coefficient, high-laser damage threshold and high optical non-linearity [4,5,6]. In addition, 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 advantages of this kind of material 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 optoelectronic devices. Amino acids are interesting organic materials for NLO applications as they contain donor carboxylic (COOH) group and the proton acceptor amino (NH₂) group in them, known as zwitterions which create hydrogen bonds.

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] have been reported. K.C. Bright et al. (2010) have reported the growth of L-alanine cadmium chloride, an organometallic nonlinear optical material which showed thermal stability up to 385 K and the dielectric studies revealed that the material was good for micro-electronic application [12]. D.Prabha et al. (2010) have successively grown L-alanine Potassium chloride semi organic single crystals. They have reported that alanine and potassium chloride molecules were arranged in alternate layers in the crystal and there was no damage of alanine structure. Hence, they also concluded that material was belonging to the soft materials since the value of the work hardening coefficient was low [13]. L. Gobinathan et al. (2015) have reported that the incorporation of the potassium in the material resulted in the slight decrease in the hardness of the L-alanine single crystals [14]. Redrothu Hanumantharao et al. (2012) have grown L-alanine lithium chloride single crystals and they have reported the NMR studies. It revealed that CH-group split to quartlet under the influence of adjacent methyl group of alanine and the methyl group split to doublet due to the

influence of single proton attached to the adjacent carbon atom of l-alanine. Also it has high SHG efficiency when compared to L-Alanine, L-Alanine acetate, L-Arginine Chloride-Arginine bromide [15].

In the present work, a semi organic non-linear optical material LAPS has been synthesized and a systematic study has been carried out. An attempt has been made to compare and study the effect of Potassium Sulphate in different proportions on the Physico - Chemical properties of L -Alanine. The lattice parameters of the crystal were determined by the Single Crystal X-ray diffraction. The morphological studies were carried out using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis (EDX). The functional groups present in the crystal were confirmed by the FTIR spectroscopic technique. The vibrational band assignments

for the grown crystals were using FTIR spectroscopic techniques in the range 400-4000 cm^{-1} . The variation of mass with the temperature was studied using the TGA and DTA. An attempt was made to study the dielectric properties of the grown crystals.

2. MATERIALS AND METHODS

Crystal growth

L-Alanine Potassium Sulphate (LAPS) was synthesized from analytical reagent(AR) grade of L-alanine (Merck, 99% AR) and Potassium Sulphate (Merck, 99% AR). L-alanine was dissolved in double deionised water. Potassium sulphate was added separately with the pure LA solution, in definite molecular ratio, LA:PS in molar weight, ((0.20:0.80), (0.40:0.60), (0.60:0.40), (0.80:0.20)) and four solutions were prepared respectively. They are denoted as LA20, LA40, LA60, and LA80 in this paper. The solutions were stirred well for five hours separately. They were filtered using high quality filter papers of pore size less than 1 mm. The filtered solutions were kept for slow evaporation. The entire process was carried out at room temperature (30°C). Tiny transparent seed crystals were observed in the experimental vessels after 12 days of evaporation. Recrystallization process was carried out in order to eliminate impurities in the LAPS crystals. Optically Good quality crystals were obtained within the period of three weeks. All the grown crystals were colorless, stable and transparent. The Photograph of as grown LAPS single crystals is presented in Figure.1

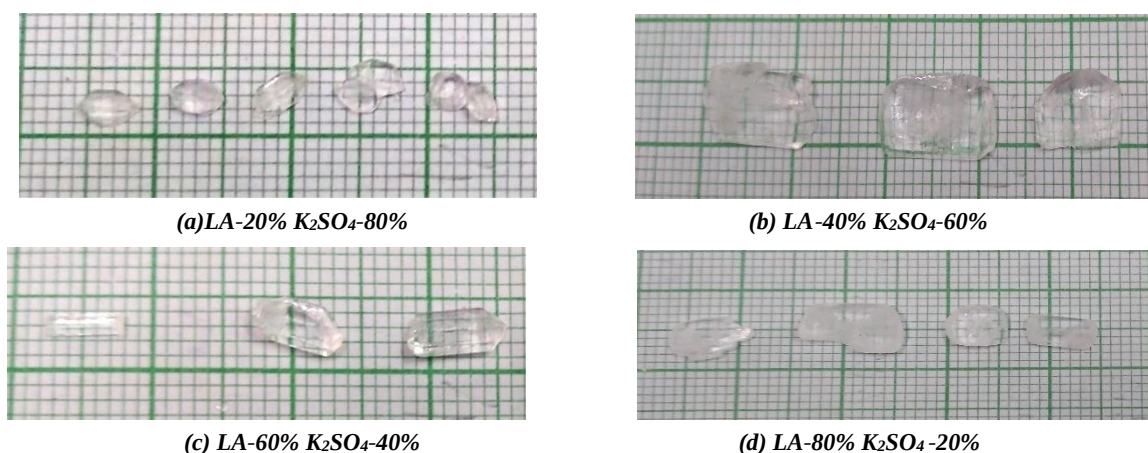


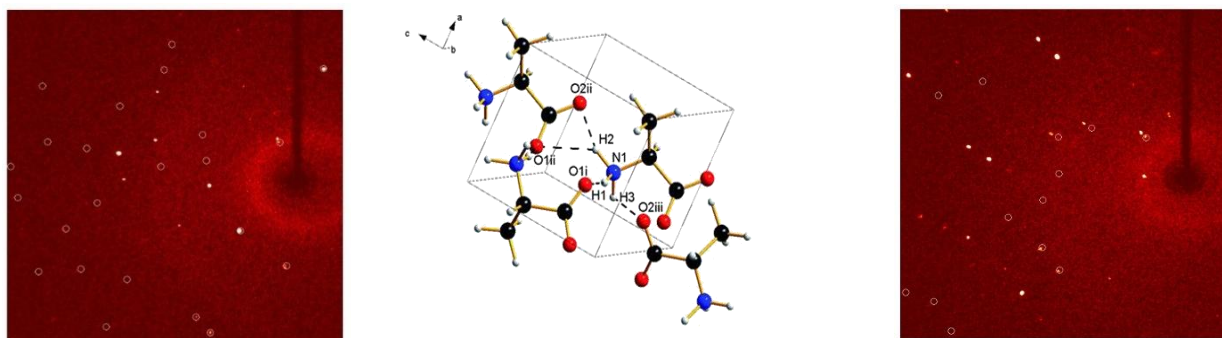
Figure. 1 -As grown LAPS single crystals (a,b,c,d)

3. RESULTS AND DISCUSSION

3.1 Single Crystal XRD studies

The grown crystals of LAPS were subjected to single crystal X-ray diffraction studies using ENRAF NONIUS CAD4 diffractometer with $\text{MoK}\alpha$ radiation ($\lambda=0.71073 \text{ \AA}$) to determine the crystal structure. The measurement was carried out at SAIF, IIT Madras, Chennai. The obtained values of cell parameters of LAPS crystals in this work are found to be in close agreement with the data reported in literature [15]. The single crystal XRD data for LAPS are provided in the Table 1. The structure of the LA crystal is confirmed to be orthorhombic and the number of molecules per unit cell is 4. The space group of LAPS crystal is $P2_12_12_1$ and this is recognized as non-centro symmetric. It is the essential

requirement for a crystal to have the Second Harmonic Generation properties. Figure. 2 represents the XRD image of LAPS and structure of crystal.



(a) LA-20% K₂So₄-80% (b) Pure L-Alanine molecular structure (c) LA-40% K₂So₄-60%
Figure. 2 -Photograph of Single crystal XRD of LAPS

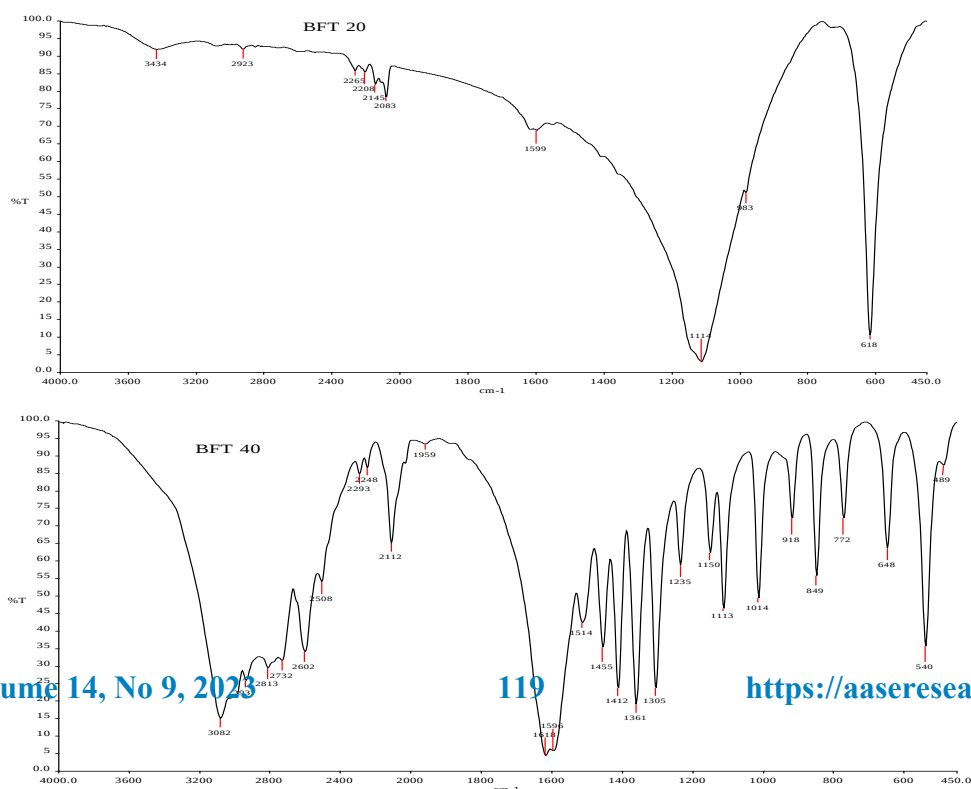
Table 1- Single Crystal XRD analysis data of LAPS

	Pure LA	LA-20% K ₂ So ₄ -80% LA20	LA-40% K ₂ So ₄ -60% LA40	LA-60% K ₂ So ₄ -40% LA60	LA-80% K ₂ So ₄ -20% LA80
Symmetry	Orthorhombic structure	Monoclinic structure	Orthorhombic structure	Orthorhombic structure	Orthorhombic structure
Lattice constants	a= 5.80 Å b=6.04 Å c=12.38 Å $\alpha=90^\circ$ $\beta=90^\circ$ $\gamma=90^\circ$	a= 5.80 Å b=7.52 Å c=10.14 Å $\alpha=90^\circ$ $\beta=90.17^\circ$ $\gamma=90^\circ$	a= 5.790 Å b=7.50 Å c=10.13 Å $\alpha=90^\circ$ $\beta=90^\circ$ $\gamma=90^\circ$	a= 5.70 Å b=7.50 Å c=10.13Å $\alpha=90^\circ$ $\beta=90^\circ$ $\gamma=90^\circ$	a= 5.80 Å b=6.04 Å c=12.38 Å $\alpha=90^\circ$ $\beta=90^\circ$ $\gamma=90^\circ$
Volume	434 Å ³	443 Å ³	439 Å ³	439 Å ³	436 Å ³

3.2 FT-IR Analysis

The presence of functional groups in the title compound was identified using the FTIR spectral analysis. The FT-IR spectra of LAPS crystals were recorded in the region 4000-400cm⁻¹ using Perkin Elmer FTIR Spectrometer at SAIF, IIT Madras, Chennai. The sample was prepared by pressing LAPS with KBr into pellet form. The spectra obtained are shown in Fig. 3.

The absorption peaks at 3083, 1618, 1514 cm⁻¹ show the presence of NH₃⁺ 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 absorptionpeak at 2111 cm⁻¹ is due to the combination band of NH₃⁺ degenerate mode and NH₃⁺ torsion. The peak at 1618 cm⁻¹ is due to the deformation of NH₃⁺. The peak at 1514 cm⁻¹of weak intensity belongs to symmetric NH₃⁺ 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 spectra of the crystals. The peak at 539 cm⁻¹ represents the COO⁻ rocking. From the Fig.3 it is seen that the FTIR spectra of LA40, LA60 and LA80 crystals are found to be similar to each other. The FTIR spectrum of LA20 crystal is distinct from the other three spectra and it can be seen in Figure.3. The vibrational band assignments for the absorption peaks of the FT-IR spectra of have been done in accordance with the data reported in the literature [16-19]. Table. 2 provides the vibrational band assignments of the corresponding crystals discussed.



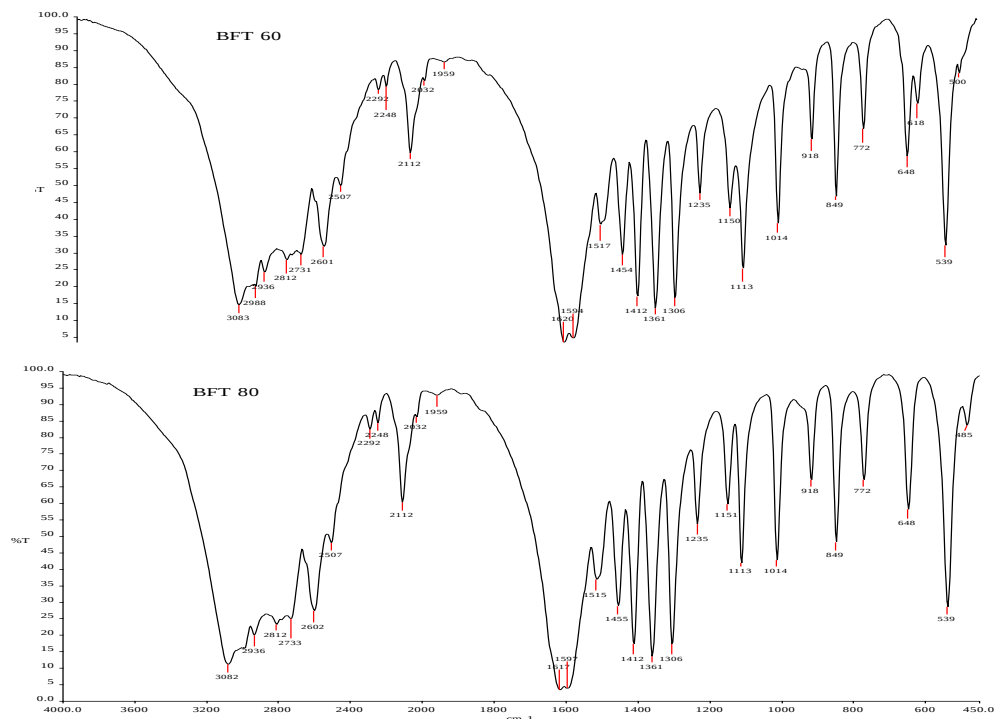


Figure. 3 - FTIR spectra of LAPS crystals

Table 2 - The vibrational band assignments of LAPS crystals

Frequency (cm ⁻¹) For LA80, LA60, LA40 crystals	Band assignment	Frequency (cm ⁻¹) For LA20 crystal	Band assignment
3083(vs)	NH ₃ ⁺ stretching	3434(w)	O-H stretching
2811(s)	C-H stretching	2923(w)	C-H stretching
2732(s)	C-H stretching	2265(w)	C-H stretching
2508(m)	C-H stretching	1599(m)	NH ₂ Asymmetric deformation
2111(m)	NH ₃ ⁺ degenerate mode and NH ₃ ⁺ torsion	1114(vs)	C-O stretching
1618(vs)	Asymmetric deformation of NH	983(m)	H-C-C-H bending
1514(s)	Symmetric deformation of NH ₃ ⁺	618(vs)	NH ₂ ⁺ symmetric bending
1412(vs)	COO ⁻ symmetric stretching	1599(m)	NH ₂ Asymmetric deformation
1306(s)	COO ⁻ symmetric stretching	1114(vs)	C-O stretching
1235(s)	COO ⁻ symmetric stretching		
1112(m)	COO ⁻ symmetric stretching		
772(w)	COO ⁻ scissoring		
539(m)	COO ⁻ rocking		

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

3.3 SEM and EDX Analysis

The results of FTIR spectral analysis of LA20 crystal kindled our interest to carry out the morphological studies of the same. So, the grown crystal LA20 (LA:PS as 20:80 molar ratio) was subjected to SEM analysis to study the surface morphology and the presence. The SEM images of the sample were recorded using Quanta FEG 200 - High Resolution Scanning Electron Microscope. To examine the surface morphology of the crystals, the transparent regions of the grown crystals were cut into a few mm and they were used for the study. At magnification of 500x and at a scale of 100µm, we see that the surface of the crystal is not smooth. The SEM micrographs at 1K and 3K magnifications presented in Figure.4 show this clearly. During the synthesis process of the material at room temperature, vacancies and feebly attached impurities are present in the lattice of the crystals formed. During SEM analysis, on the application of 20 kV, intrinsic defects are produced resulting in certain plateaus and valleys in the crystal surface. Due to high temperature, such roughness develops in the surface. The increase in Potassium Sulphate concentration brings such nature and it is clearly observed from SEM analysis.

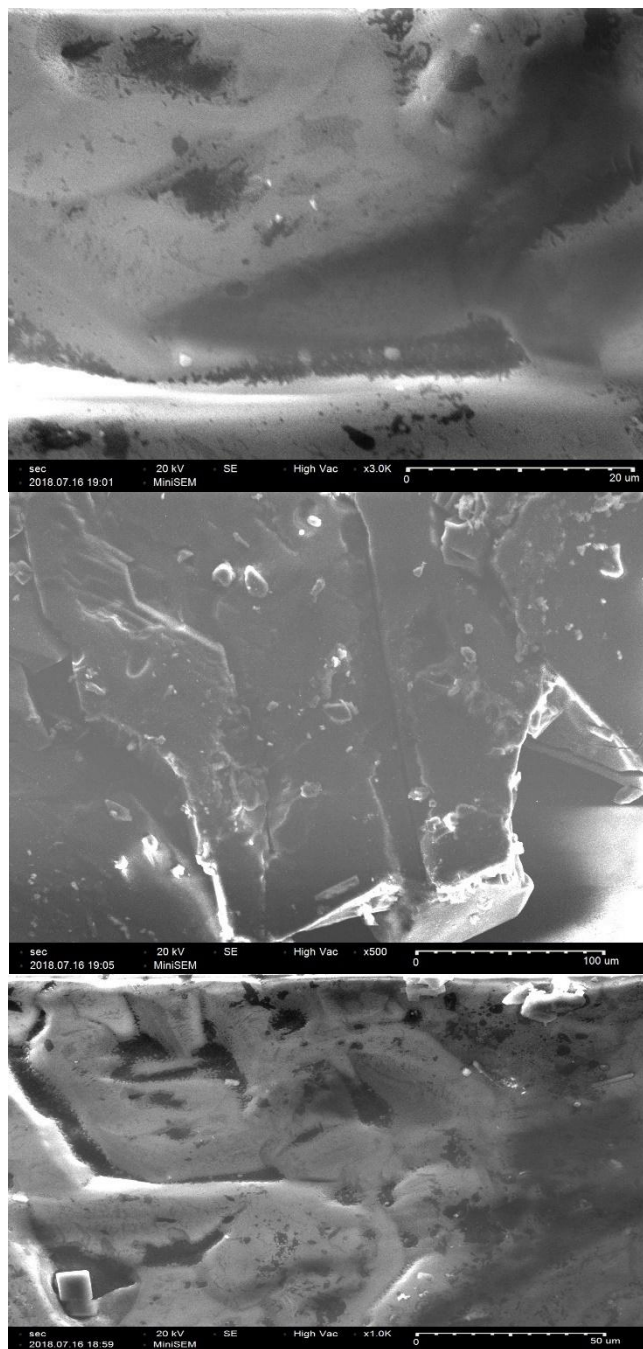


Figure. 4 - Magnification of SEM micrograph of LA20 crystals

Energy Dispersive X-ray analysis was used to obtain information regarding the chemical composition of the grown crystal. The EDX spectrum of the LA20 crystal was recorded using Quanta FEG 200 - High Resolution Scanning Electron Microscope and it is presented in Figure.5.

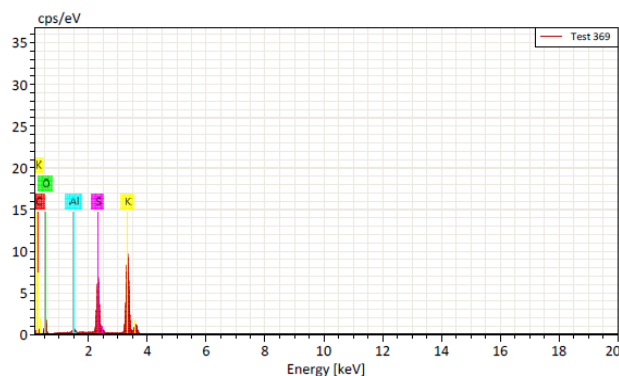


Figure 5- EDX spectrum of LA20 crystals

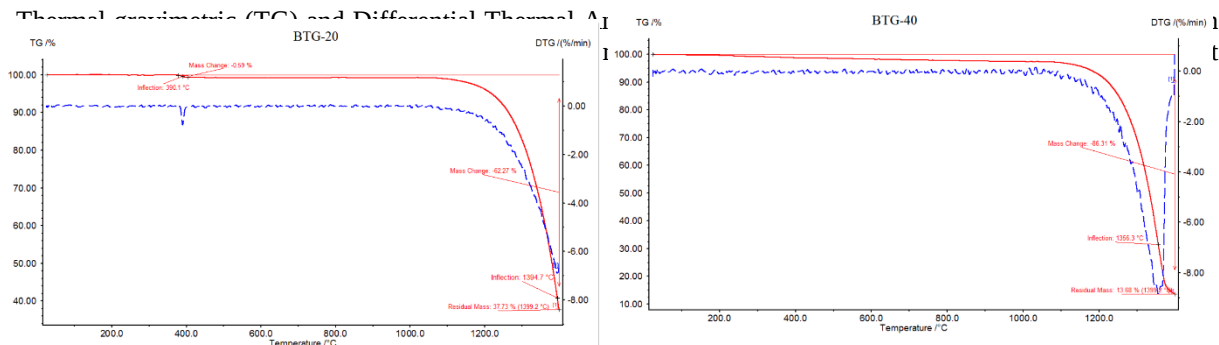
In this technique, a pencil beam of X-rays is incident on the sample material. The energy of X-rays emitted by the sample is due to the energy difference between the two shells of the atomic structure of the material. Hence the X-rays emitted by the sample carry the information about the elemental composition of the material and the percentage of elements in the sample are given in Table 3.

Table 3 - EDX Quantification Table of LA20 crystals

Element	Weight %	Atomic %
Carbon	23.10	33.68
Oxygen	47.66	52.17
Aluminum	1.13	0.73
Sulfur	8.46	4.62
Potassium	4.62	8.80
Total	100.00	100.00

3.4 Thermal studies

Thermal gravimetric (TG) and Differential Thermal Analysis (DTG) were performed on the LA20 crystals using a BTG-20 and BTG-40 thermogravimetric analyzer.



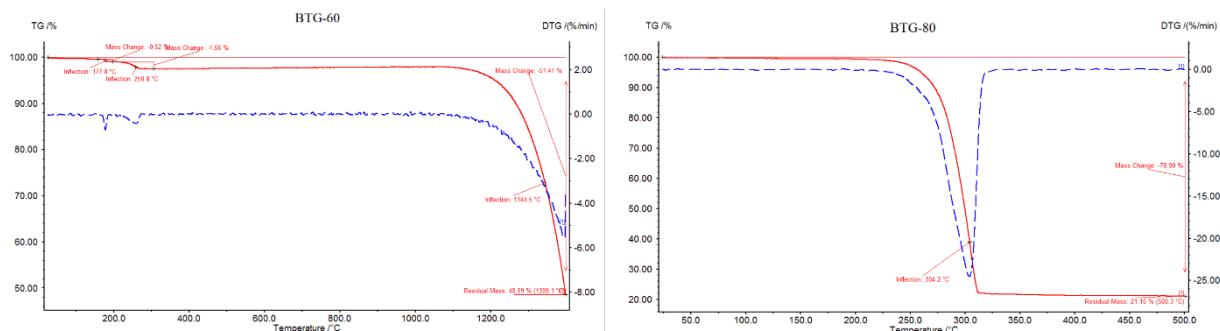


Figure6 - Thermo Gravimetric Analysis Spectra of LAPS crystal

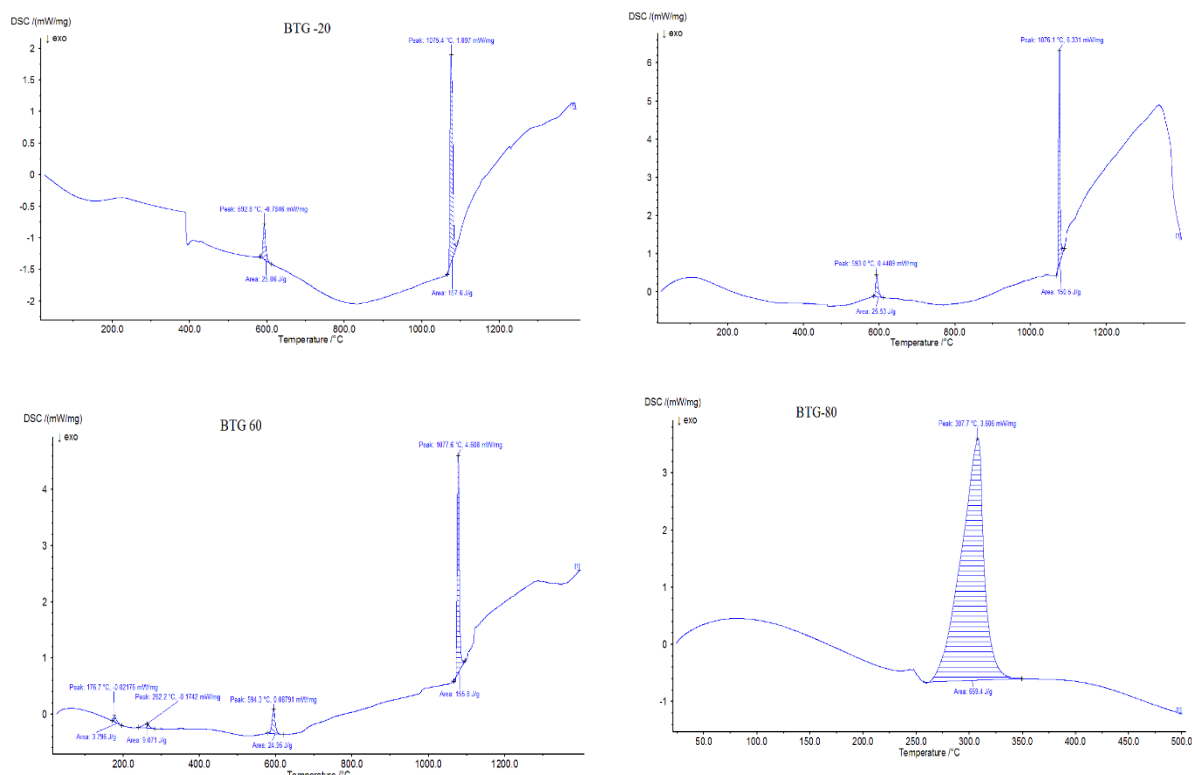


Fig 7 - Differential Thermal Analysis curves of LAPS crystals

The TGA and DTA traces of the LAPS crystal are shown in Figure.6 and Figure.7 respectively. From the TGA curves, it is clear that the crystals LA20, LA40 and LA60 are stable till 1075 °C. The TGA curve of the crystal LA80 shows that the crystal is stable till 304 °C and the weight loss of 78.9% corresponds to the decomposition of L-Alanine. From the DTA graph, irreversible endothermic transition is observed at 1075 °C in the crystals LA20, LA40 and LA60 which is attributed to the melting point of Potassium Sulphate. The endothermic peak at 1394°C shows 64.27% decomposition of the crystals. The endothermic peak at 307.7 °C in the DTA graph of LA80 crystal is due to the melting point of L-Alanine. The results of DTA are being consistent with the TGA data. The sharpness of the endothermic peaks shows the good degree of crystalline nature of the samples. The decomposition of LA80 crystal happens around 304 °C. The major decomposition of LA20, LA40 and LA60 crystals occur at around 1075 °C and hence they are stable up to that temperature. Hence these crystals can be exploited for many applications.

The kinetic parameters namely, activation energy (E), entropy(ΔS), enthalpy (ΔH), Gibb's free energy (ΔG) of activation were obtained from the first step decomposition of LAPS single crystals. The Thermo-Gravimetric based model, Coats-Redfern method has been used in the present work for the approximation of kinetic parameters[20]. The present study claims its significance for being the maiden attempt in the thermo-analytical studies of semi-organic crystal, LAPS.

3.4.1 Thermo-analytical studies using 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).

$$\frac{d\alpha}{dt} = K f(\alpha) \quad \text{---- (i) and}$$

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

$$\ln K = \ln A - [E/RT] \quad \text{---- (ii)}$$

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

$$\alpha = [(W_0 - W_t)/(W_0 - W_\infty)] \quad \text{---- (iii)}$$

where, W_0 is the initial weight of the sample, W_t is the weight at time 't' and W_∞ is the final weight. $\frac{d\alpha}{dt}$ is the rate of reaction and $F(\alpha)$ is the mathematical expression in α describing the kinetic and mechanical step.

For $n = 1$

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

This equation is similar to linear equation $Y = MX + C$.

Where

$$Y = \log[-\log\{(1-\alpha)/T^2\}], M = (-E/2.3032R), C = [\log(AR/\beta e)(1-2RT/E)] \text{ and } X = 1/T$$

where n is the order of reaction, R is the gas constant, E is the activation energy of the reaction and β is the linear heating rate. A graph between $\log[-\log(1-\alpha)/T^2]$ against $1/T$ results in a straight line of slope $-E/2.303R$. The slope is found by least square fitting method. The value $\log[(AR/\beta e)(1-(2RT/E))]$ is constant for most of the values of E and the temperature range over which the reaction occurs.

The values of E , the activation energy of the reaction and A , Arrhenius constant or frequency factor can be calculated from these equations.

$$E = 2.303 \times R \times \text{slope} \quad \text{---- (v)}$$

$$(AR/\beta e)(1-2RT/E) = e^{\text{intercept}} \quad \text{---- (vi)}$$

From the above equation, other thermodynamic parameters can be calculated using the formulae given below.

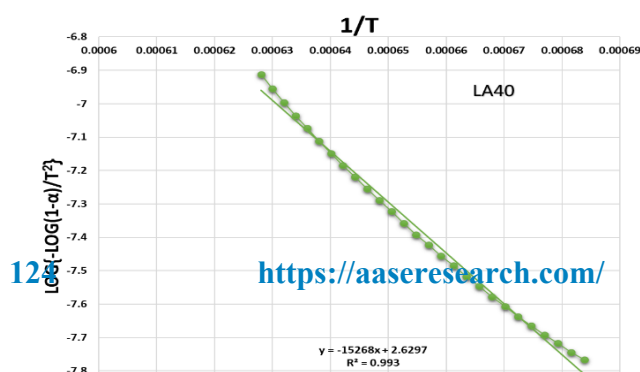
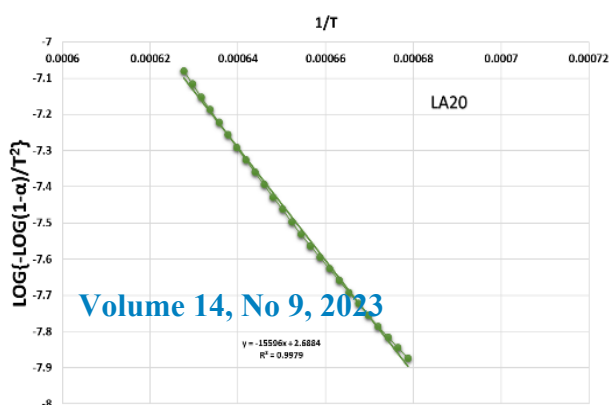
$$\text{Entropy, } \Delta S = 2.303R \log(Ah/kT_{1/2}) \quad \text{---- (vii)}$$

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.

$$\text{Enthalpy, } \Delta H = E - 2RT \quad \text{---- (viii)}$$

$$\text{Gibb's free energy, } \Delta G = \Delta H - T\Delta S \quad \text{---- (ix)}$$

The equations (i)-(ix) are solved for the TGA data of the decomposition of LA20, LA40, LA60 and LA80 crystals and the corresponding Coats-Redfern plots for LAPS crystals are projected in Figure.8. The parameters such as E , A , ΔS , ΔH and ΔG corresponding to the endothermic peak 1075 °C are calculated for LA20, LA40, LA60 crystals. For LA80, the same is done for 307 °C peak. The computed values of the thermodynamic parameters mentioned above are presented in Table 4.



Thermodynamic parameters	LA 20	LA 40	LA 60	LA 80
--------------------------	-------	-------	-------	-------

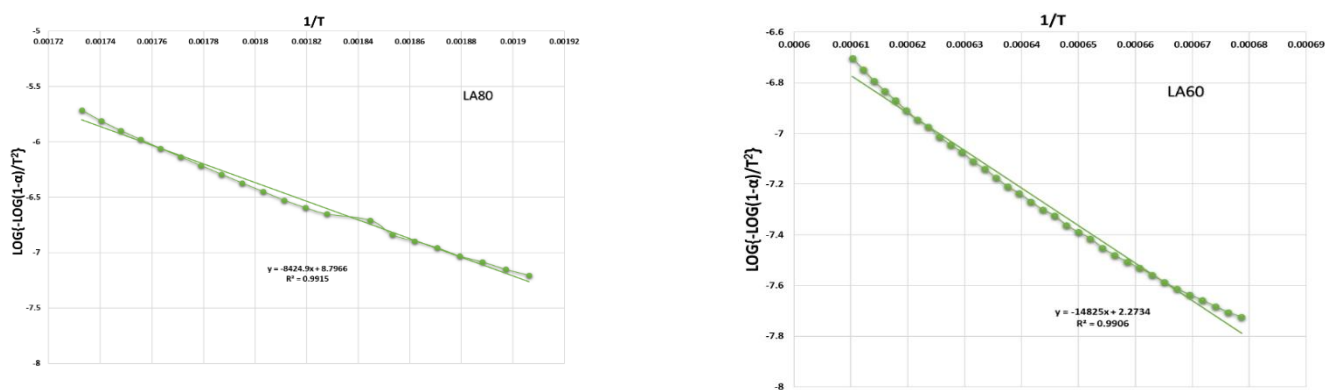


Figure 8 - Coats –Redfern plots for LAPS crystals

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 activation energy of a particular reaction determines the rate at which the reaction will proceed. The higher the activation energy, the slower the reaction will be. The activation energy increases with the increase in molar proportion of Potassium Chloride in the crystals. The negative entropy in LA20, LA40 and LA60 indicates that the disorder in the system has decreased. The value of enthalpy shows that the reaction is endothermic and the Gibb’s energy being positive indicates that the reaction is endergonic and non-spontaneous in the forward direction.

Table 4 - Kinetic and thermodynamic parameters of LAPS crystals using Coats-Redfern relation

Activation Energy(E) (kJmol ⁻¹)	298.63	292.35	283.85	161.31
Arrhenius Frequency Factor (A)	5.6 x 10 ⁹	4.7 x 10 ⁹	2.03 x 10 ⁹	3.6 x 10 ¹⁵
Entropy (ΔS) (JK ⁻¹ mol ⁻¹)	-68.59	-69.93	-76.95	54.38
Enthalpy (ΔH) (kJmol ⁻¹)	289.70	283.42	274.91	158.82
Gibb's Free Energy (ΔG) (kJmol ⁻¹)	363.43	358.58	357.64	142.50

3.5 Dielectric studies

A study of dielectric properties of solids gives idea about the electric field distribution in them. The frequency dependence of these properties gives great insight into the material applications. The HIOKI 3532-50 HITESTER LCR meter characterized the dielectric properties of the suitably cut and polished LAPS crystals of known dimensions. The opposite faces of the crystals were coated with silver to ensure good ohmic contact. The samples were placed between two copper electrodes to form a parallel plate capacitor. The dielectric measurements were carried out by changing frequency from 50 Hz to 50 MHz for different temperatures (305, 348, 383 and 413K). The dielectric constant of the crystals has been calculated using the equation,

$$\epsilon_r = Ct/A\epsilon_0 \quad \text{--- (x)}$$

Essentially, ϵ_r is the measure of how easily a material gets polarized in the presence of external electric field. By knowing the value of capacitance (C) of the sample, thickness (t) of the sample, permittivity of free space (ϵ_0) and area of cross section (A) of the sample, the value of ϵ_r can be calculated.

The variation of dielectric constant as a function of log frequency at different temperatures for LAPS crystals is shown in Figure. 9.

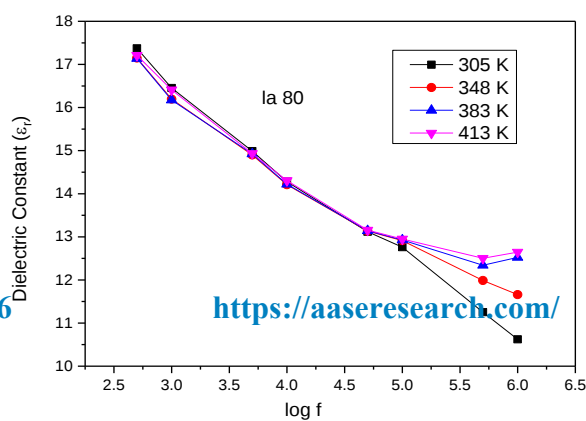
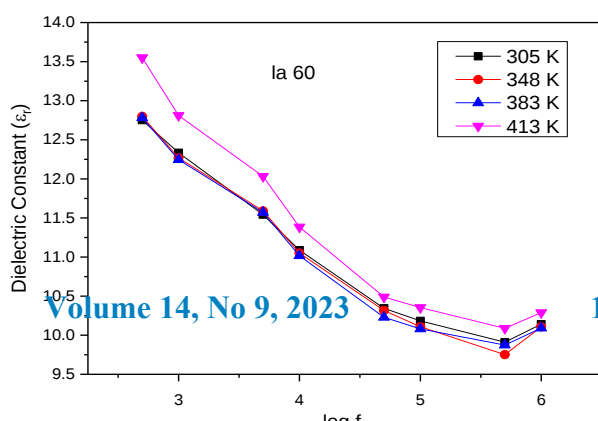
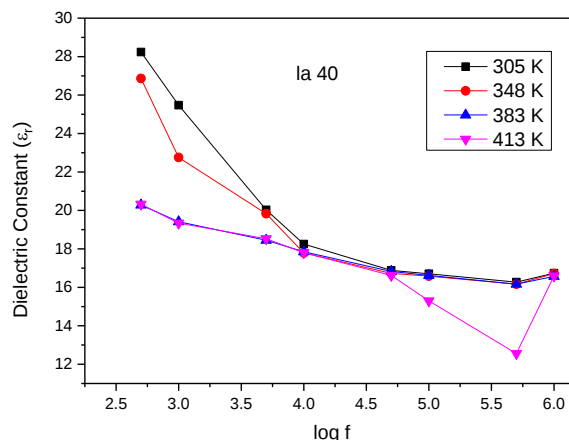
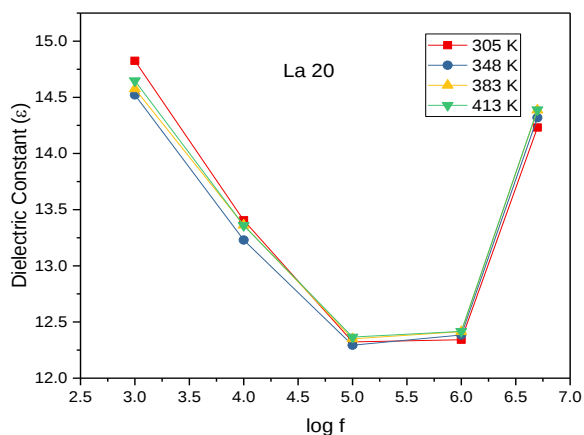


Figure9- Variation of dielectric constant with frequency

As the frequency increases, the dielectric constants decrease exponentially and attain lower value at high frequency. At lower frequencies, the electronic (α_e), ionic (α_i), orientational (α_o) and space-charge polarization (α_s) will be high and there is a gradual decrease of these polarizations at high frequencies. Decrease of dielectric constant with frequency suggests the presence of higher space charge polarization of the material in the low-frequency region[21]. The investigated crystals also follow the same pattern. However, a sudden throw at higher frequency region of LA20 may be due to the increase in potassium concentration. A material with low dielectric constant will have less number of dipoles per unit volume. The increase in dielectric constant with increase in temperature was due to the presence of space-charge polarization near the grain boundary interfaces, which depends on the purity of the sample[22]. The variation of dielectric constant with varying temperature is meager in LA20, LA60 and LA80 crystals. This suggests that these samples possess high chemical homogeneity[23].

Dielectric loss (δ) is the loss of energy that goes into heating a dielectric material in a varying electric field. Dielectric losses depend on frequency and the dielectric material and it has been calculated using the relation,

$$\tan \delta = D / \epsilon_r \quad \text{---- (xi)}$$

where D is the dissipation Factor and ϵ_r is the dielectric constant.

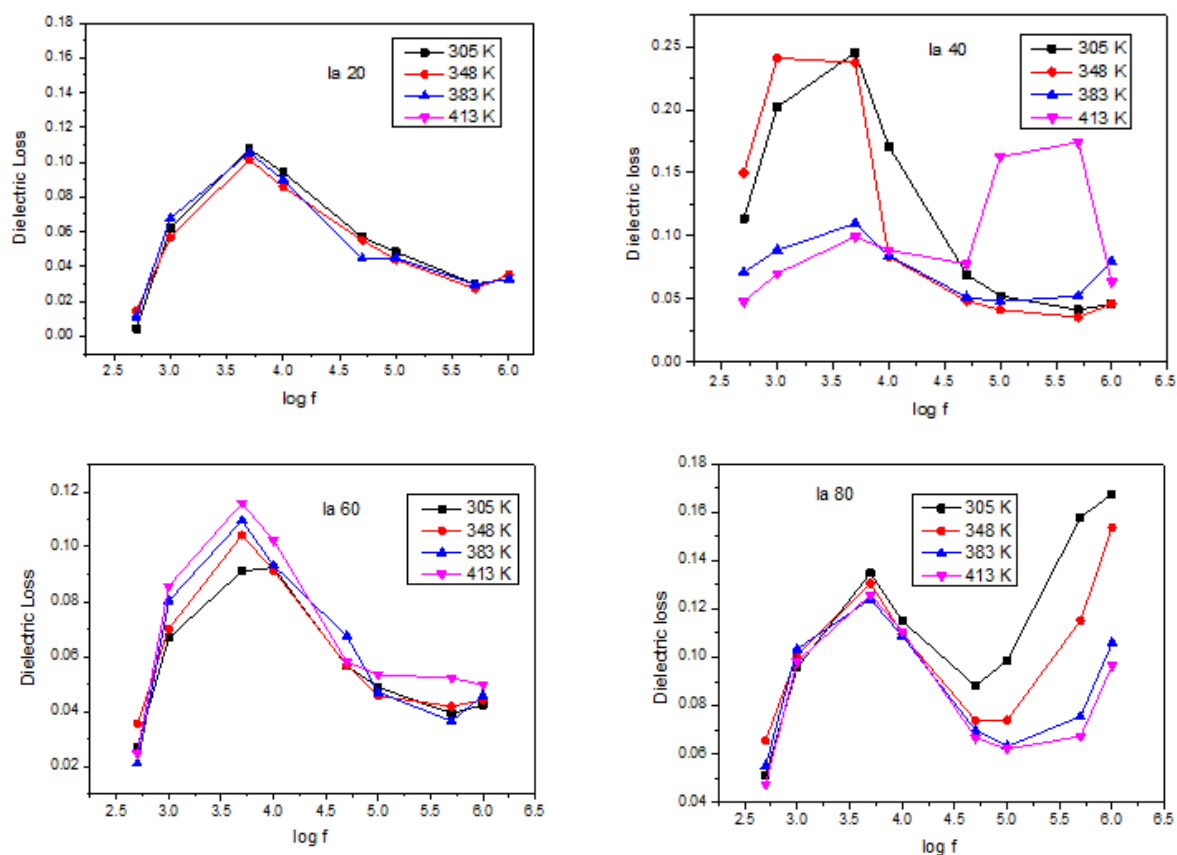


Fig10- Variation of Dielectric Loss of LAPS crystals

Dielectric losses were examined as a function of log frequency at different temperatures for LAPS crystals and indicated in Figure. 10. It is clearly seen from the curves that similar to dielectric constant, dielectric loss of the

crystals also is strongly dependent on the frequency of the applied field. The low value of dielectric loss at high frequencies for LA20, LA40 and LA60 crystals show that these crystals possess lesser defects [24].

4. CONCLUSION

Good quality semi-organic single crystals of L-Alanine Potassium Sulphate were grown by slow evaporation technique. The precursors were taken in definite molar ratios and crystals were grown. Unit cell parameters were evaluated by single crystal X-ray diffraction studies, which confirmed that the grown LA40, LA60 and LA80 crystals belong to orthorhombic system. Also the X-ray studies reveal the monoclinic structure and the crystalline nature of LA20 crystals. The various functional groups and their vibrational interactions of the grown crystals are confirmed by Fourier Transform Infrared analysis. The surface analysis of LA20 crystal was done and the percentage of elements of the grown crystal was confirmed by elemental analysis. The thermal behavior of LAPS crystals was studied using TG/DTA analysis. The increase in the concentration of Potassium Sulphate in LAPS crystals has enhanced the thermal stability of the grown crystals. The kinetic parameters such as activation energy (E), entropy(ΔS), enthalpy (ΔH), Gibb's free energy (ΔG) of activation were calculated using Coats-Redfern relation. The variation dielectric constant and dielectric loss of grown crystals was studied as a function of frequency at different temperatures and the results were discussed. Thus the grown LAPS crystals with noticeable dielectric properties and good thermal stability would be applicable as potential material for photonic and electro-optic devices.

REFERENCES

- [1] Prasad P.N, Willams. D.J. Introduction to nonlinear optical effects in molecules and polymers; Washington DC,1991.
- [2] Marder, S R; Sohn, J E, Stucky, GD., Materials for nonlinear optics, American chemical society, Washington, DC,1991
- [3] IttyachanR and SagayarajP, Journal of Crystal Growth, vol. 249, pp. 553–556, 2003
- [4] Saleh B.E, Teich. A, Fundamentals of photonics, Wiley, Newyork, 1991.
- [5] Madhavan J, Aruna S, Ambujam K, Cryst.res.technology, 41, 1211-1216 (2006).
- [6] Narayanan Bath M. Et al.Journalof Crystal Growth, 236, 2002, pp 376–38
- [7] Wojciechowski, Ozga K. Reshak A H, Materials letter, vol.64, no 18, pp.957-959,2010.
- [8] Reshak A H, S.Auluck, D. Stys,Journal of material chemistry, vol.21,pp.17219,2011.
- [9] M.Victorantony raj, J.Madhavan, Archives of Physics Researchers, 2011, 2(1),pp160-168.
- [10] ShanthiD,Selvarajan P, Optik - International Journal for Light and Electron Optics,Volume 125, Issue 11, pp 2463-2722 (2014).
- [11] Shanmugam P and Pari S, Journal of Chemical and Pharmaceutical Research, 2015, 7(5), pp 44-53
- [12] Bright K C, Freeda T H, Physica B,405(2010) 3857–3861
- [13] Prabha D and Palaniswamy S, Journal of chemistryVol.3, No.3 (2010), 517-524
- [14] Gobinathan L, Boopathy KDe5r Pharma Chemical, 2015, 7(11),362- 367
- [15] RedrothuHanumantharao, S. KalainathanSpectrochimicaActa Part A 86. (2012) 80– 84
- [16] Colthup N B, Wiberly S E and Daly L H, Introduction to Infrared and Raman Spectroscopy, 2nd Ed., Academic press, Newyork, 1975.
- [17] Gandhimathia P,Shanthib J, International Journal of Engineering Research &Technology,Vol. 2,2013
- [18] Socrates G, Infrared and Raman characteristics group frequencies, 3rd Ed., Wiley, Newyork, 2000.
- [19] Bellamy L J, The Infrared spectra of complex molecules, 3rd Ed., Chapman and Hall, London, 1975.
- [20] CoatsA W, Redfern J P,Kinetic parameters from thermos-gravimetric data. Nature 201, 68–69 (1964).
- [21] Senthil Pandian M, Ramasamy P, Journal of Crystal Growth.312, 413–419 (2010).
- [22] ShanmugaSundaramM,Vijayalakshmi V,Journal of Crystal Growth,506,122-126,(2019)
- [23] Hiremath V A, Venkataraman A,Bull.Mater. Sci. 26(4), 391–396 (2003)Loganayaki, M &Murugakoothan, P.Asian Journal of Chemistry. 23. 5089-5091(2011).

CITE AN ARTICLE

It will get done by IJESRT Team