Thermal, Dielectric, and Optical Studies of Non-linear Semi organic L-Leucine Doped Potassium Hydrogen Phthalate Crystals

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Abstract

Single crystal of L-Leucine doped Potassium Hydrogen Phthalate have been produced using slow evaporationprocedure. The study of formed crystal was performed with Single crystal X-Ray diffraction (XRD), Powder XRD diffraction, Dielectric, Vicker's Micro hardness, TG/DTA, Laser Damage Threshold Second Harmonic generation (SHG), Photoluminescence characteristics Fourier Transform Infrared (FTIR) and UV-Visible spectroscopy. XRD technique was used to investigate the structural differences between doped and undoped crystals. FTIR spectroscopy was used to identify functional groups. The crystal optical band gap was calculated using the transmittance of the doped potassium hydrogen phthalate(KHP) crystal. The TG-DTA findings show that the material has high thermal stability. Vicker's hardness test was used to determine mechanical strength of formed crystal. The Kurtz powder technique has confirmed the second harmonic generation. It was observed to be more compared to KDP. The photoluminescence technique also noticed the similar results.

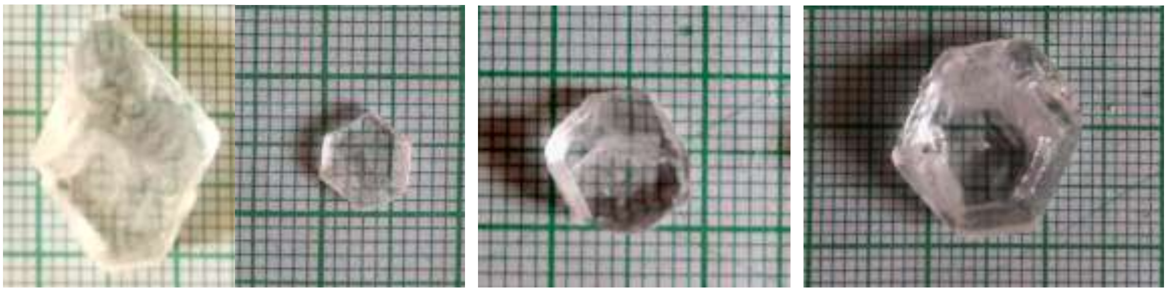
Keywords: Crystal, doping, L-Leucine, optical, polymer.

1. Introduction

The growth of optoelectronic and photonic technologies has resulted from the exploration for NLO material with good transparency in recent years [1]. Potassium hydrogen phthalate (KHP), in X-Ray spectroscopy, is an analyzing material [2, 3]. Piezoelectric, elastic, pyroelectric, and nonlinear optical characteristics are all found in KHP. KHP crystallize into orthorhombic system with non-centro symmetric space groups Pca21 and lattice parameter are noted to be a= 9.605A0, b=13.331A0, c= 6.473A0. Surface morphological analyses such as SEM and etching are better suited to KHP's perfect cleavages (010) plane. KHP crystal has already been employed as substrate material for formation of a highly orientated conjugated polymer film with high nonlinear susceptibility. [4]. Crystals in family of Amino acidare now significant in the field of non-linear optics. Since doping affects different properties of formed crystals, it's critical to verify doping in KHP crystals. The present study in which the amino acid L-Leucine (LL) (C6H13NO2) (0.05,0.1, and 0.15mol percent) was included as a debasement into parent KHP and impact of contaminations on optical, structural, mechanical and thermal characteristics was contemplated and detailing was done with this goal in mind.

2. Material and Methodology

At room temperature, crystals of KHP were produced using slow evaporation solution growth approach using double distilled H2O as solvent. At first, saturated KHP at room-temperature was created. As a dopant, the amino acid L-Leucine (LL) was chosen. The dopant concentration in the solution was changed between 0.05, 0.1, and 0.15mol%. For four hours, the undoped and LL doped KHP saturated solutions were continuously stirred. A Whatman filter paper was used as filter to obtain the homogenous solution. Separate beakers with perforated sheets were used to store the contents. The crystals were created by evaporating the solvent over a twenty-five to thirty-day period. The crystals that had grown were collected and subjected to characterization tests. Figure 1 shows photographs of LL doped and undoped KHP crystals.



(a) (b) (c) (d)

Fig.(1).Formed crystals of (a) undoped and ((b) 0.05, (c) 0.1& (d) 0.15 mol %) L-Leucine doped crystals.

2.1 Single crystal X-ray diffraction study

The developed undoped and doped KHP crystalswere exposed to single crystal XRD examination. The lattice parameter and cell volume of KHP undoped and LL doped crystals are given in Table1. It is seen from X-ray diffraction data that both undoped and LL doped KHP crystal have a place in orthorhombic system. The lattice parameters of undoped KHP are in excellent concurrence along with the detailed qualities. There is a negligible difference in the lattice parameters acquire from single crystal X-beam diffraction on case of doped and undoped KHP crystals. On account of doped KHP crystals, slight variation in estimations of lattice parameter and cell volume are recognized. The alteration in the lattice parameters is because of the consolidation of L-Leucine molecules into the crystal lattice.

Table1. Single crystal XRD data of doped & undoped KHP crystals

Lattice Parameter	**Undoped KHP**	**0.05mol% LL doped KHP crystals**	**0.1mol% LL doped KHP crystals**	**0.15mol% KHP LL doped crystals**
a(Å)	9.625	9.616	9.606	9.517
b(Å)	13.31	13.319	13.306	13.296
c(Å)	6.460	6.471	6.479	6.405

2.2 Powder X-Ray Diffraction Studies

XRD was performed in developed crystals, to examine impact of doping on KHP doped crystals with L-Leucine. The Powder XRD pattern was noted using X'Pert pro along with Cu Kα1 radiation (wavelength = 1.54060 A0) for phase examination.Powder XRD pattern of formed crystal illustrated in Figure 2. Powder XRD pattern of undoped KHP is well agreement with the JCPDS PDF (31-1855) [5]. The very much characterized peaks at explicit 2θ values in the powder XRD pattern of developed samples indicate high crystallinity of developed crystals [6, 7]. UNIT CELL programming package was utilized to confirm the lattice parameters from the powder XRD data.

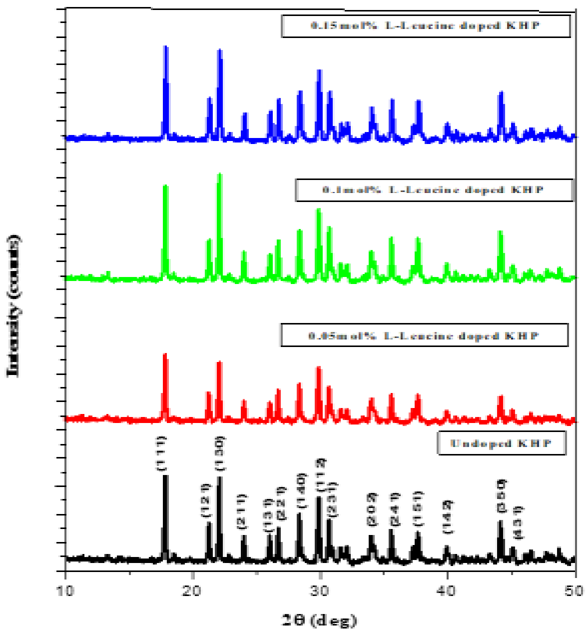


Fig (2). KHP crystal's Powder XRD pattern; (a) undoped, (b) 0.05mol% LL, (c) 0.1mol% LL, (d) 0.15mol% LL doped crystals

2.3 FTIR Spectral Analysis

The FTIR spectral studies were performed to find the chemical bonding and sub-atomic structure of material. The FTIR spectra were noted utilizing Perkin Elmer spectrum in range four hundred-four thousand cm-1 by using KBr pellet approach. The formed crystal's FTIR spectrum are in Figure 3. This study includesanalysis of bending, stretching, twisting and vibrational modes in a molecule to identify the sample's functional groups [8]. At the point when infrared radiation collaborates with a sample, a segment of the occurrence radiation is consumed in explicit wavelengths. The observed vibrational wave numbers and assignments of FTIR band frequencies for undoped and LL doped KHP crystals are presented. The Carbon=Carbon ring stretching is around 1489 cm^{-1} for both doped and undoped samples. The peaks 3442 cm^{-1} and 3435 cm^{-1} for LL (0.05 & 0.1mol %) doped KHP when compared to undoped sample. This region can also be taken as evidence for doping of amino acids.

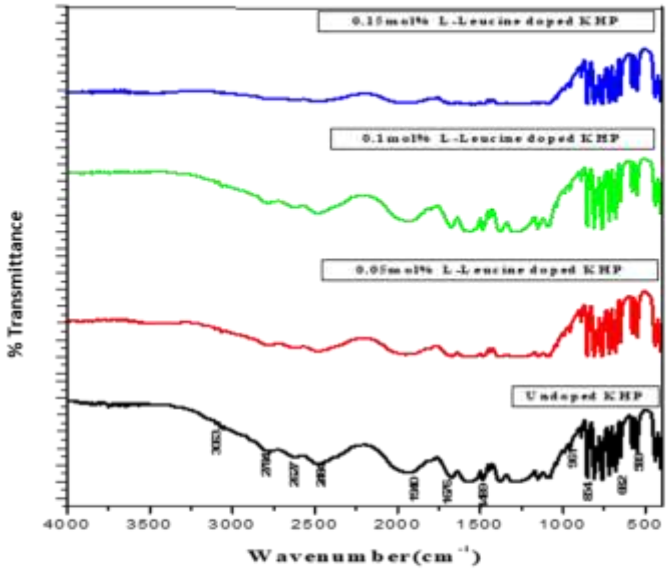


Fig 3. FTIR spectrum of KHP crystal; (a) undoped, (b) 0.05mol% LL, (c) 0.1mol% LL, (d) 0.15mol% LL doped crystals

2.4 Optical Analysis

The UV-Visible spectrum give data about molecule structure due to the fact the UV absorption involves in transport of electron in π and σ orbitals from ground level to better power states. Low absorptions, sufficient and high-quality transmittance within the entire visible and near infrared location of the spectra of grown crystals can be viewed from the graphs. From the graph, it's also noticed that the transmittance percentage of doped KHP doped crystals are more desirable than the transmittance percent of undoped KHP. The recorded UV- Visible transmittance spectrum of KHP undoped and L-Leucine doped crystals are illustrated in Figure 4. From figure, it is clear that KHP crystals both (doped and undoped)have their UV cutoff at approx. 300 nano meters. This is because of n to π transition of carboxyl functional group's carbonyl group [9,10]. Thegraph of difference of $(\alpha h\nu)^2$Vs (hν) for grown crystals is presented in discern Figure 4(a). These plots are recognized as the Tauc's plot. They exceptional out the accurate optical band gap price with the aid of the extrapolation of the linear part.

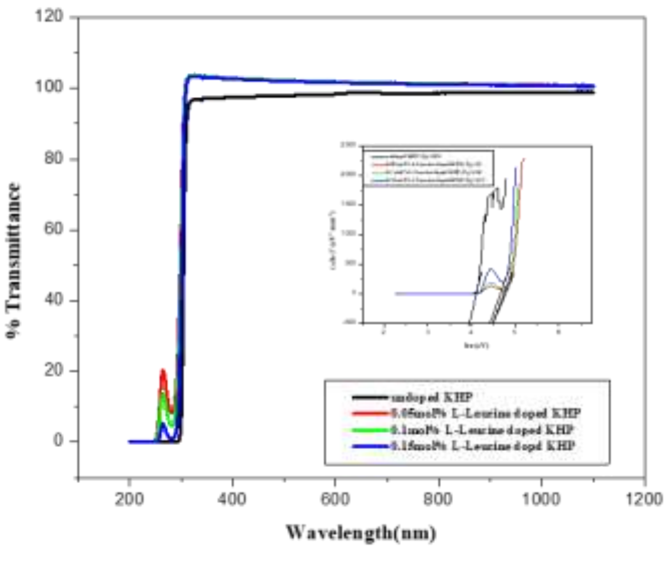


Fig 4 KHP crystal's UV-NIR spectrum and Tauc's plot (a) undoped, (b) 0.05mol% LL, (c) 0.1mol% LL, (d) 0.15mol% LL doped crystals

2.5 Photoluminescence Study

Photoluminescence depth is fantastically depending on crystalline and crystal's structural perfection. Formed crystals of undoped and (0.05, 0.1 and 0.15mol %) LL doped KHP are scanned at400-800 nano meter. The noted spectra of patternare proven in Figure 5. For 346.87 nm which is excitation wavelength, the found emission bands lie among 450 - 600 nm. KHP Undoped and

LL doped crystals confirms the emission of green fluorescence, which recommends that they are exceptional for optical nonlinear application. Then PL force is lately decreased inside high wavelength vicinity. It can be assigned to enormously low barrier for rotation of 2 carboxyl groups of critical Carbon-Carbonbond [11, 12, 13].

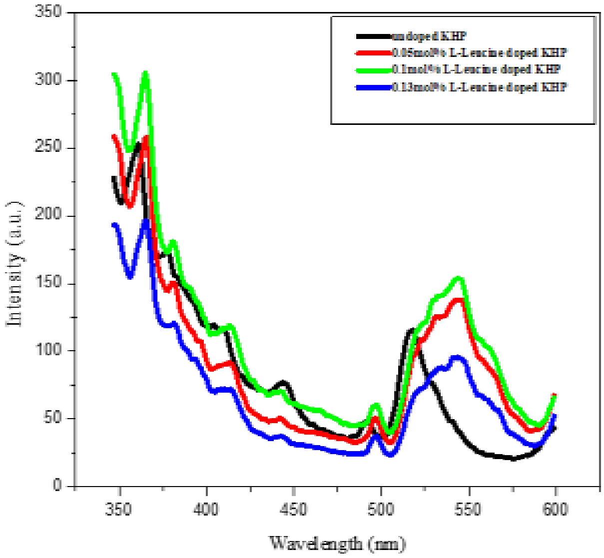


Fig.5 PL wavelength versesintensity of(a) undoped, (b) 0.05mol% LL doped KHP, (c) 0.1mol% LL doped KHP, (d) 0.15mol% LL doped KHP crystals

2.6 SHG studies

The formed crystals were analyzed with Nd: YAG laser with wavelength of roughly 1064nano meter used to validate their NLO characteristic. The powder sample was exposed to this high-intensity beam.

Table 2. SHG efficiency of the undoped and doped L-Leucine doped KHP crystals

Samples	SHG Efficiency
Undoped KHP	0.65
0.05mol% LL doped KHP	0.92
0.1mol% LL doped KHP	1.28
0.15mol% LL doped KHP	1.44

The crystal's 2ndharmonic generation characteristics are confirmed by green light emission. 0.701mJ/pulse was energy of input beam, with width of a pulse 6nano meter and a repetition rate of 10Hz.The SHG performance is anticipated with recognize to conventional KDP and listed in Table 2.The increment in SHG effectiveness of amino aciddoped KHP crystal may be because of interplay of amino acid with KHP through H-bond [14,15]. This beneficial circumstance can be chargeable for boom in SHG effectiveness on doping of L-Leucine..

2.7 Hardness Studies

The micro hardness values had been found from system $H_v=1.8544P/d^2$ Kg/mm^2. Where, Vickers hardness is Hv, d is diagonal length and applied load of the indentation influence is P[16]. The maximum load of the Vickers hardness variety is discovered to be 100gm. It is discovered that hardness number raise with growth in load and it is obvious that KHP doped crystal have negative correlation with indentation effects. In existing work, the hardness variety will increase because of the addition of L-Leucine in KHP crystals. The value of hardness as function of load is depicted in Figure 6.

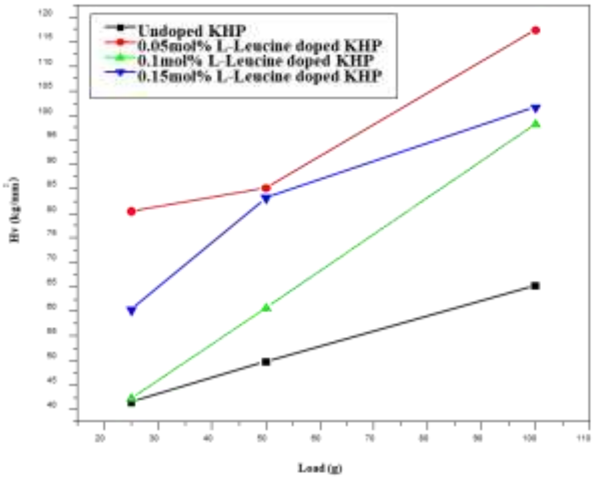


Fig. 6 Change of number of Vickers hardness with applied load for undoped and LL doped KHP crystal

2.8 Yield Strength

The micro hardness number (H_v) is related to yield strength (σ_y) via the subsequent equation. $H_v= 3\ \sigma_y$. The yield energy is described as the pressure at which a preterminal quantity of malformation occurs. Since n is located to be extra than 2, yield energy of the material can be constituted out following relations. Yield strength $(\sigma_y) = (H_v/3)\ (0.1)^{n-2}$

The change of yield electricity with load for grown crystals are presented inside Figure 7. It is observed that values of yield energy of grown crystal increase with the carried-out load and for this reason the grown crystals have especially excessive mechanical energy.

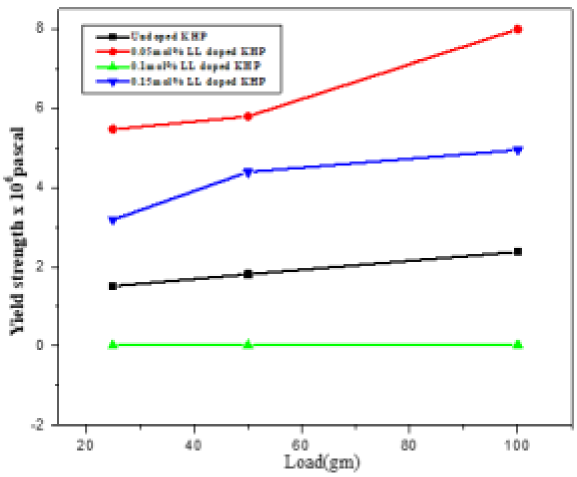


Figure (7) change of yield strength with load for undoped and LL doped KHP crystal.

2.9 Dielectric Studies

Dielectric studies are carried out to investigate response of samples to an applied discipline and to decide various electric properties inclusive of dielectric regular (ε_r), dielectric loss (tan δ) and conductivity at extraordinary temperatures. Figure 8 indicates the plotof dielectric constant Vs frequency of area applied for undoped and LL doped KHP crystal. It can be determined that the frequency of implemented subject will increase with the decrease in dielectric constantand for excessive frequency region it remainssomewhat constant. The dielectric constant of undoped KHP crystal decreases than doped KHP crystals. Also, it is discovered that value for dielectric constant reducesas quantity of doping of L- Leucine increase.

Figure 9 reveals the variant dielectric loss (tan δ) with frequency for L-Leucine doped KHP crystals. From plots, we can infer that frequency increase with decrease in dielectric loss. Also, dielectric loss reduces as quantity of doping increase within crystal.

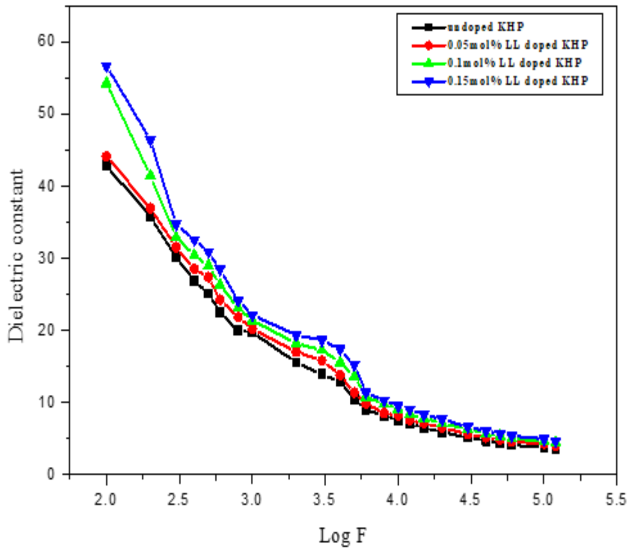


Figure (8) The graph of changing dielectric constant with log frequency for LL- doped KHP crystal

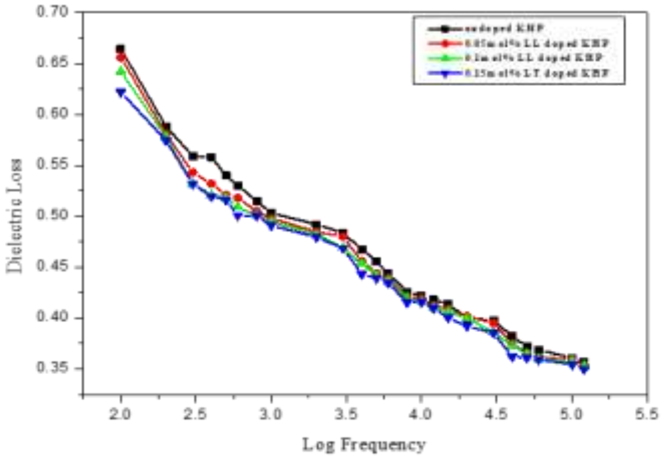


Figure (9) The graph of difference of dielectric loss with log frequency for LL- doped KHP crystal

2.10 AC conductivity of grown crystals:

Differences of AC conductivity with temperatures for KHP undoped and LL doped crystals are proven in Figure 10.

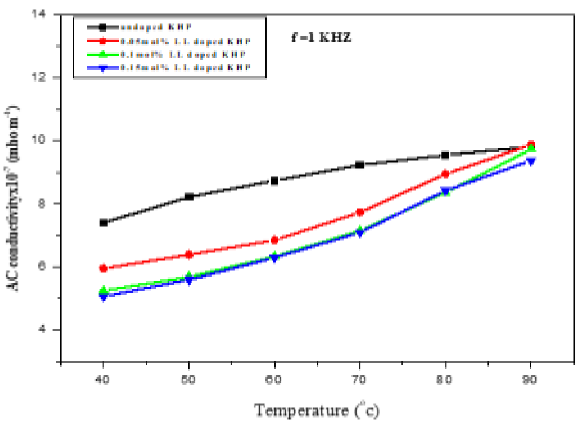


Figure (10) Change of AC conductivity with Temperature at 1KHZ for undoped and LL doped KHP crystal.

From the above graph, its miles observed that AC conductivity value increase with increment of temperature for grown crystals because of opportunity of weakening of hydrogen bond while growing the temperature.

2.11 Laser Damage Threshold Measurement

The laser damage threshold changed is determined for the undoped and LL doped KHP crystals by the usage of single shot laser mode. For the nonlinear optical application, one of the maximum critical issuesin preference of substance is its resistance and tolerance to laser to work as a tool for NLO programs. The LDT decide the usage of the following components, $P = E/\pi\tau r^2$

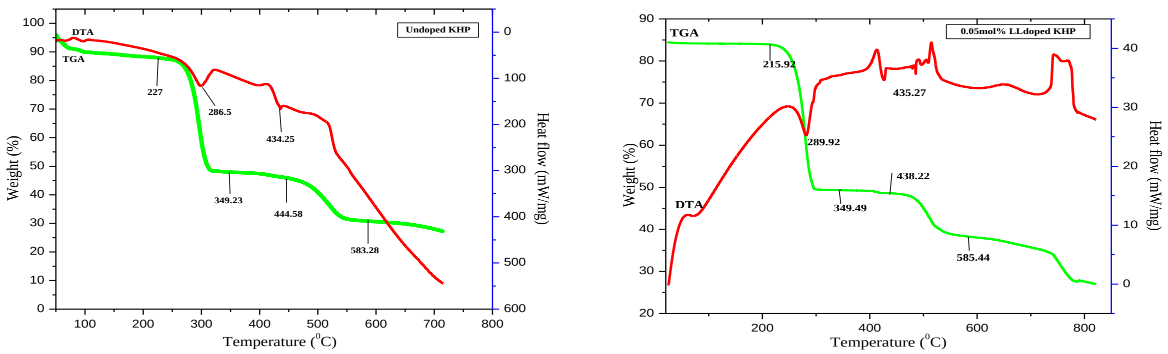
Where E is the energy required in milli joule, τ is the response time in nano seconds, and r is radius of spot in milli meter. The LDT value observed and entire electricity which make damage on crystal surface are given in Table 3. The values of LDT of the samples are discovered to be dependent on hardness and thermal behavior.

Table 3 Laser Damage Threshold values for KHP undoped and LL doped crystals

Samples	**Input Energy (mJ)**	**LDT Value (GW/cm^2)**
KHP Undoped	84	0.347
0.05 mol% LL doped KHP	86	0.356
0.1 mol% LL doped KHP	92	0.42
0.15 mol% LL doped KHP	96	0.45

2.12 Thermal Analysis

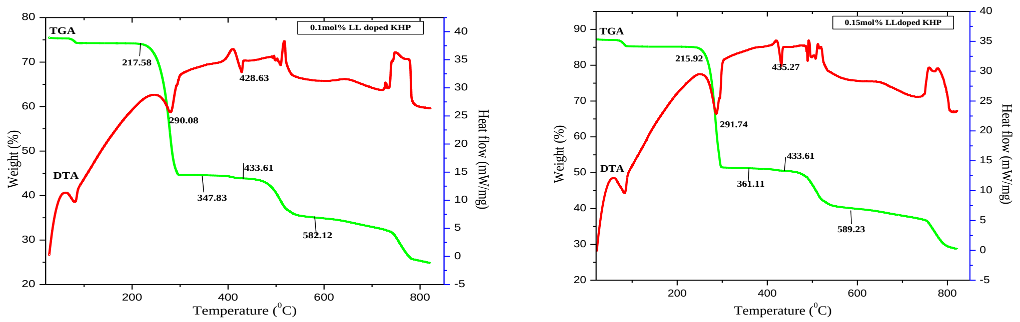
The thermal houses of the LL doped KHP crystals have been studied by the use of TG/DTA studies. This research was done for the samples to discover the weight change (TG), Energy alternate (DTA) and numerous endothermic and exothermic transitions inside the samples with the trade of temperature.



(a) **(b)**

Fig 11(a &b) TG/DTA curves of undoped and 0.05mol% LL doped KHP crystal

The formed crystals are kept in fully closed chamber with nitrogen waft environment which is controlled at 5°C/minute heating rate. TG/DTA curvefor undoped and LL doped KHP crystal are depicted in 11(a) figure.The TG thermo gram exhibits that decomposition starting from 0.05mol% LL doped KHP at 215.92°C and increase to 349.49°C as proven in picture 11(b).The TG thermo gram shows that decomposition begins for 0.1mol% LL doped KHP at 217.58°C and raised to 347.83°C as depicted in 11(c) figure.The TG thermo gram exhibits that decomposition begins for 0.15mol% LL doped KHP at 215.92°C and increase to 361.11°C as depicted in 11(d) figure.



(c) **(d)**

Fig 11(c &d) TG/DTA curves of 0.1 and 0.15mol% LL doped KHP crystals

3. Conclusion

The KHP L-Leucine doped crystals were formedat room temperature by solution growth method. From single crystal XRD, the unit cell constant is confirmed and Powder XRD measurements display that fairly defined Bragg's peaks at unique 2θ angle and all prominent peaks were listed. Marginal exchange inside the unit cell parameter is changed into determined ones, which indicate that doping would not regulate KHP's crystal structure. This confirm that the crystal goes with orthorhombic crystal system. The data is confirmed by FTIR spectrum. From the UV-VIS spectra, the transparency variation of LL doped KHP is determined between 350-1100 nm. Altogether, theoptical transmission percentage will increase with increment in doping of L-Leucine in KHP crystals. As the doping level of LL doped KHP crystal improved the SHG performance increased. Looking at PL research, KHP undoped and LL doped crystal verifythe emission of green fluorescence, which in turn indicate that they may be great for nonlinear optical programs.For the Vickers micro-hardness of KHP undoped and LL doped crystal, it's analyzedthat hardness will increase with loadsand, itindicates that dopedKHP crystal can exhibit reversed indentation impact. From TG/DTA data, undoped and LL doped KHP crystal shows that as degree of doping increase, the crystals can become thermally more stable than undoped crystals.

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References

[1]. Shujun. Z, jihua.X, zhilin.X, nuclear fusion and plasma physics, vol.13, 61 (1993)

[2]. Zho.Q.L, J.Appl. Cryst. 27, 283(1993)

[3]. Miniewics. A, barkiewics. S, Adv. Mat. Opt. Elect, 2, 157 (1993)

[4]. Van Enckevort WJP, Jetten LAMJ.J crystal Growth. 1982; 60: 275

[5]. N. Balamurugan, M. Lenin, P. Ramasamy, Mater, Lett, 61(2007)1896

[6].Kanchana,P.Elakkinakumaran. A, Sekar. C, spectrochemm. Acta, part A. 112.21.2013

[7].Mulley. G.G, Rode.M.N and Pawar.B.H, ActaPhysicaPolonica, A 116 (2009) 1033.

[8]. Khopkar.S.M, " Basic concepts of Analytical chemistry", Wiley Eastern, New Delhi (1984).

[9]. Rajesh, P. Ramasamy, Physica B 404(2009) 1611

[10]. K. Sangwal, Additives and crystallization Process, john wiley and sons Ltd, 2007.

[11]. Earnet. C. M, Anal. chem. 59(1984) 1471-1475

[12]. Aravindan. A, Srinivasan.P, crystal.Res.Tech.11,10977 (2007)

[13].Aravindan. A, Srinivasan.P, Vijayan. N, Gopalakrishnan. R, Ramasamy. P, spectrochem,

Acta part A 71(2008) 297- 30

[14]. Parimaladevi .R, Sekar.C, Krishnakumar.V, spectrochem. Acta,Part A. 75.617.2010

[15] .RedrothuHanumantha Rao &Kalinathan S 2013, Optik 124 pp 2204.

[16].Kanagasekaran T, Mythili P, Srinivasan P, Shailesh Sharma N, Gopalakrishnan R 2008, Materials Letter 62 pp 2486