Growth and spectroscopic, thermal, dielectric and SHG studies of L- threonine doped KDP crystals

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Potassium Dihydrogen Phosphate (KDP) crystals are one of the most popular crystals used for Non-linear Optical (NLO) applications. Most of amino acids also exhibit NLO property; therefore, the effect of doping of one of the amino acids, L – Threonine, in KDP crystals has been investigated. Pure and L – Threonine doped KDP crystals were grown by slow solvent evaporation solution growth technique. For obtaining doped crystal, 0.3 and 0.4 weight percent solutions of L – Threonine was added to aqueous solution of KDP. Good quality transparent crystals were obtained within 8 to 10 days. Doping of amino acid in grown crystals was confirmed by paper chromatography, C H N analysis and FT – IR spectroscopy studies. The powder XRD suggested the single phase nature and the unit cell parameters were not altered due to doping. Thermal stability of the grown crystals was studied by employing TGA. It was observed that on increasing the amount of doping the decomposition of sample occurred slightly at lower temperature than that of the pure KDP crystals. The dielectric constant and the dielectric loss of L-Threonine doped KDP crystals were lower than the pure KDP crystals. Increment in the values of the second harmonic generation (SGH) efficiency was noticed in doped crystals with comparison to the pure KDP crystals. The percentage optical transmission increased with increasing the doping of L- threonine in KDP. It was found that the doping of L – Threonine does not alter the physical properties of KDP by large extent, alike in the case of other amino acids. The results are discussed.

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Keyword: Crystal growth, NLO Materials, SHG efficiency, Dielectric study, FT-IR Study, Thermo-gravimetry

1. Introduction

Potassium dihydrogen phosphate (KH_2PO_4- KDP) and its isomorphous deutereted form, DKDP (KD_2PO_4), are popular due to their applications in frequency converters, electro-optic switching and modulators [1,2].Mechanisms of linear and non-linear optical effects of KDP crystals have been explained [3] . In order to get good quality crystals rapidly, many techniques have been introduced by several workers [4-7].

Several authors have doped KDP crystals by KI, NaI and Au^+ [8], ammonium compounds [9] and urea and thiourea [10]. It was found that the doping enhance electrical conductivity of KDP crystals. Attempts have been made to study the coloring and habit modification of dye KDP crystals as a function of dye concentration and super-saturation [11] and the distribution of dye in KDP crystals [12].The effect of swift heavy ion (SHI) irradiation on dye doped KDP crystals is studied by Kumaresan [13]. It was found that the NLO efficiency increases in dyes doped KDP crystals after Li^{3+} irradiation. Since all of amino acids, except glycine, exhibit NLO properties; several attempts have been made to dope various amino acids into KDP crystals. Pure and L-arginine doped KDP crystals have been characterized and it was found that L-arginine increased the second harmonic generation (SHG) efficiency and it was dependent on doping concentration in KDP [14]Recently, three different amino acids, namely, L-Glutamic acid, L-Valine and L-Histidine, were doped in KDP crystals and it was found that the SHG efficiency increased in order of L-Histidine doped KDP > L- Valine doped KDP > L-Glutamic acid doped KDP > pure KDP [15].The present study is a part of the extensive studies being carried out on the effect of different amino acids doping on the properties of KDP. In that regard, the effect of doping of amino acid L– Threonine in different concentration in to KDP crystals and its effect on the thermal stability, dielectric properties, SHG efficiency and the percentage optical transmission of grown crystals is reported.

2. Experimental Technique

2.1 Crystal growth

Due to good solubility of parent material KDP as well as dopant amino acid in water, slow solvent evaporation technique was employed to grow pure and doped KDP crystals. The solubility curve of KDP in double distilled water was experimentally confirmed with the available one in the literature. The doping of L- Threonine into KDP was achieved by adding 0.3 and 0.4 wt % solution into KDP solution. The mixture was thoroughly stirred for 8 h for homogenization. Good quality seed crystals were harvested in the conventional manner. Best seed crystals of respective doping were selected and placed in appropriate solution for growth. The vessel containing the solution was closed with perforated cover and kept in a constant temperature bath at 35 ^{0}C to allow slow evaporation of the solvent. .

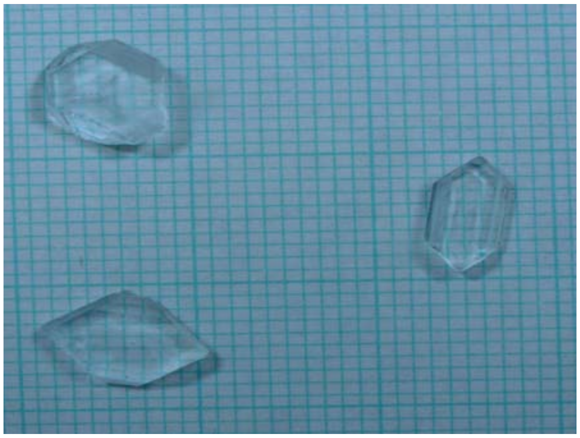


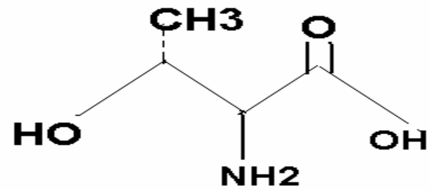
Fig. 1. A photograph of 0.4 % L– Threonine doped KDP crystals.

2.2 Characterization

The FTIR spectra were recorded on BRUKER IFS 66V FTIR spectrometer in the range from 400-4000 cm^{-1}. Paper chromatography was carried out by using nin – hydrine. The C H N analysis was performed on HARAEUS RAPID MODEL C, H, N, and O ANALYZER. Powder XRD study was carried out on PHILIPS X'PERT MPD system using Cu K_α radiation. The TGA was performed on NETZSCH Geratebau GmbH from room temperature to 900^{o}C at a heating rate of 10^{o}C/min in nitrogen media. The dielectric characteristics of the samples were studied using Agilent 4274A LCR meter in the frequency range from 500 Hz to 1 MHz. The UV-Vis spectra of pure and doped crystals were recorded on as grown single crystalline samples in a conventional manner using PERKIN ELMER LEMBDA-19 Spectrophotometer. For the measurement of SHG efficiency, the Kurtz powder method was used by illuminating the powdered samples with fundamental (1064 nm) of a Q – switched mode – locked Nd : YAG laser with input pulse of 2.7 mJ [16].

3. Results and discussion

Amino acids are promising materials for NLO applications. Complexes of amino acids with inorganic salts are considered to be novel materials for SGH properties and they are found , most of the times, to be as promising as KDP or better than it[17,18]. However, the NLO properties of L–arginine diphosphate [19],L–threonine phosphate monohydrate[20] ,L–arginine perchlorate [17], L– threonine dinitrate [21], and many other forms of L– threonine have been investigated. In the present investigation the doping of L-threonine is done in order to engineer the properties of KDP crystals. L-threonine is having structural formula as follows:



L-Thrionine

L-threonine is an α-amino acid with chemical formula HO_2 CCH $(NH)_2$ $CH(OH)CH_3$. Together with serine and tyrosine, threonine is one of the three proteinogenic amino acids bearing an alcohol group. The hydroxy side chain can undergo O-linked glycosylation. With two chiral centers, threonine can exhibit four possible stereoisomers or two possible diastereomers of L-threonine. However, the name L-threonine is used for single enantiomer (2S, 3R)-2-amino-3-hydroxybutanoic acid. [22]. L-threonine exhibits nonlinear optical properties and because of this crystals of pure L-threonine and synthesized compounds of L-threonine have been reported earlier. Optical and mechanical properties of urea L-threonine is reported [23]. The effect of pH, thermal, structural, dielectric, spectral, electrical and thermo-mechanical and NLO properties of crystals of L-threonine have been carried out by various workers [24-26].

Figs. 2(a, b, c) show the powder XRD patterns of pure KDP crystals, 0.3 % L– Threonine doped KDP crystals and 0.4 % L– Threonine doped KDP crystals, respectively. The unit cell parameters were calculated by using the software powder X. The unit cell parameters are listed in table 1.

Table 1. Unit cell parameters of pure and L-threonine doped KDP crystal.

Samples	Lattice Parameter (Å)		Cell Volume (Å^3)
	A = b	c	
Pure KDP Crystal	7.457	6.976	387.91
KDP + 0.3% L-Thrionine	7.455	6.974	387.44
KDP + 0.4% L-Thrionine	7.457	7.265	387.44

From Figs. 2 (a, b, c) one can notice that the doped crystals are slightly distorted with comparison to the pure KDP crystals. This may be due to the strain on the lattice by doping of L-threonine molecules.

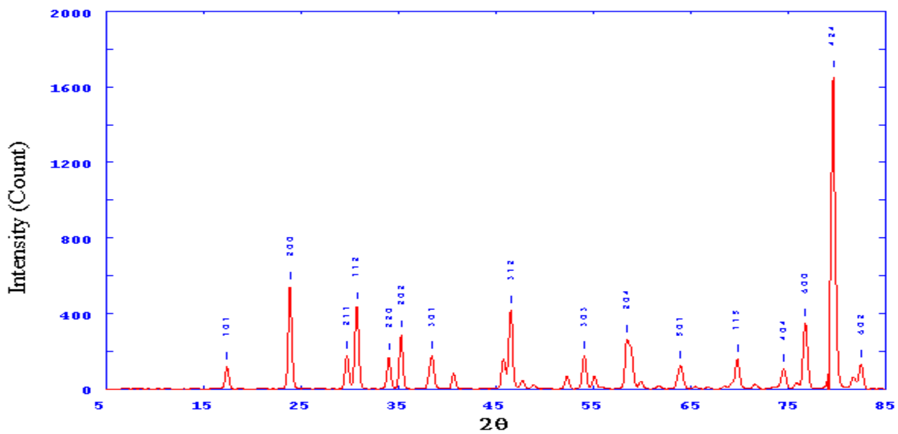


Fig. 2 (a) (Powder XRD pattern of Pure KDP)

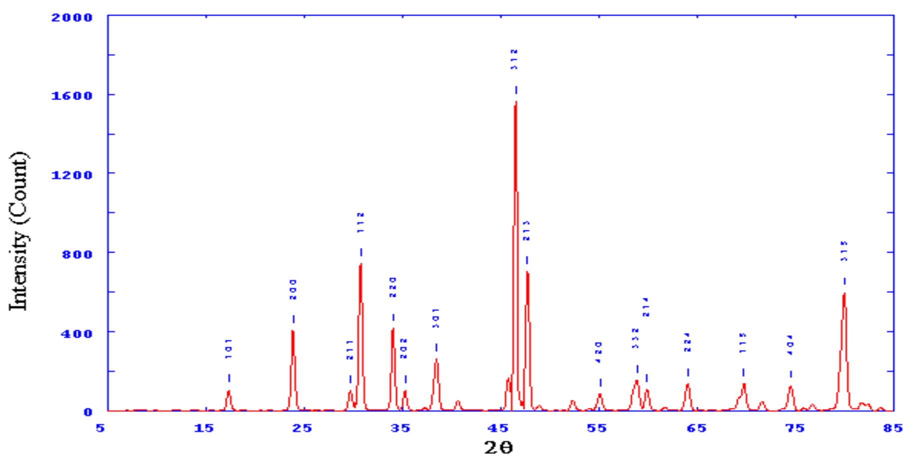


Fig. 2. (b) (Powder XRD pattern 0.3 % L Threonine - KDP).

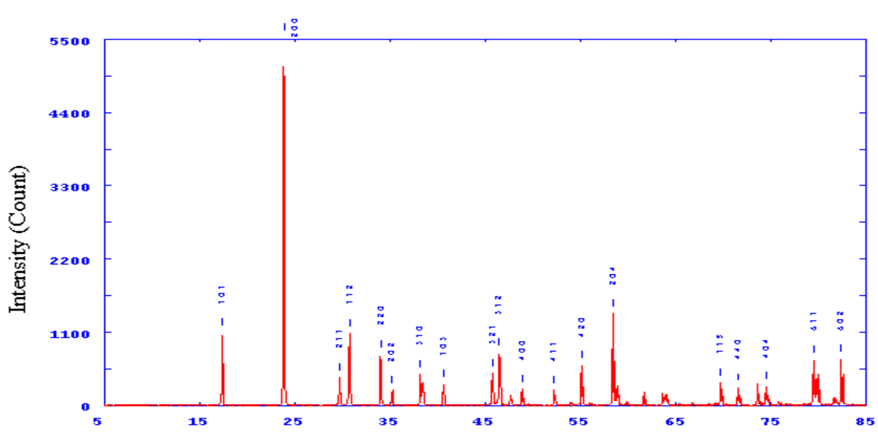


Fig. 2. (c) Powder XRD pattern 0.3 % L Threonine - KDP

The FT–IR spectra of 0.4 % L– Threonine doped KDP crystals are shown in figure (3).The broad envelopes observed between 2300 and 3600 cm^{-1} are mainly due to P–OH stretching of H_2PO_4, O–H stretching of COOH and water of crystallization, N–H stretching of NH_3^+, C–H stretching of CH_2 and CH. The broadness is generally considered to be due to hydrogen bonding interaction of $H_2PO_4^-$, $COOH^-$ and NH_3^+ with adjacent molecules. The C=O stretching and -C = NH_4 stretching are revealed by minor absorption peak within 1750 cm^{-1}. The CH_2 bending attributes the absorption at 1300.9 cm^{-1}. The absorption occurring at 1099.4 cm^{-1} and around 910.3 cm^{-1} are due to P–OH stretching. Intense absorption observed at 536.2 cm^{-1}, 435.9 cm^{-1} and 413.7 cm^{-1} are due to P–OH deformation. From spectrum of doped crystals, one can easily conclude that L– Threonine doping was successfully achieved. Usually the absorption bands 3450-3700 are due to O-H stretching. The broad envelopes around 3250-3280 are due to hydrogen bonded N-H stretching. In earlier studies, it has been found that the weak interaction of the dopants with one of the O-H groups of KDP and possible entry of dopants into the lattice sites of the crystal. This leads to the decrease in the frequency of O-H from 3600 to 3395.5 cm^{-1} and confirms the nonlinear optical nature in pure and doped crystals [27] .The paper chromatography of dissolved crystals using nin-hydrin exhibited purple spot, which is a clear indication of the presence of amino acid in the crystal.

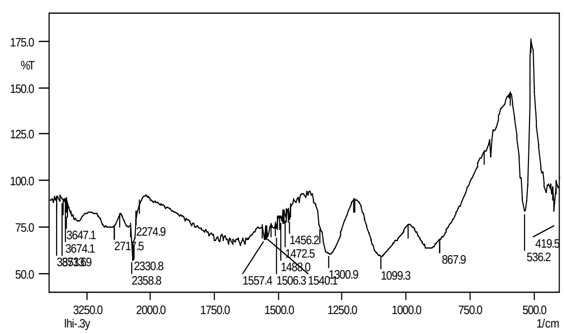


Fig. 3. FT – IR Spectrum of 0.4% L – Threonine doped KDP.

Fig. (4) shows the UV-Vis spectra of pure and doped KDP crystals. It can be noticed from the figures that as the doping of L –threonine increases in KDP crystals, the percentage transmission increases and the UV cut off frequency are not getting affected due to doping. The optical performance of KDP crystals improves on doping of L-threonine.

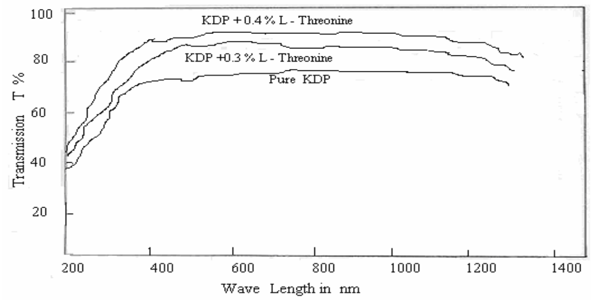


Fig. 4 (UV – Vis Spectra of pure and L – Threonine doped KDP crystals).

Fig. (5) indicates the variation of the dielectric constant with frequency of applied field for pure and doped KDP crystals, for pure and doped KDP crystals, which suggests that as the frequency increases the value of dielectric constant decreases. Higher space charge polarizability was found in the low frequency region. This suggests that the dipoles varying with the applied field can not comply with the field after certain frequency and they exhibit sharp decrease in the value, which has been discussed earlier by several workers [28, 29]. It is also found from figure (5) that the value of dielectric constant decrease as the doping increases in the crystals. Figure (6) is the variation of dielectric loss with frequency of applied field, which exhibits the same nature as shown in figure (5) for the variation of dielectric constant with frequency. It is also seen from figure (6) that as the doping increases the dielectric loss decrease, which indicates that the doping decrease the dielectric loss. The occupation of the dopant molecule in the crystalline lattice may be influencing polarization mechanism and reducing the dielectric loss.

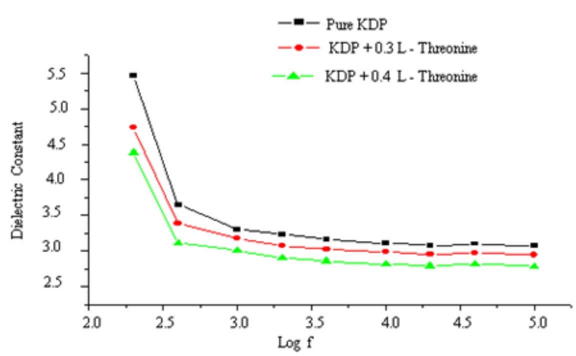


Fig. 5. Plots of dielectric constant versus frequency of pure and L – Threonine doped KDP crystals.

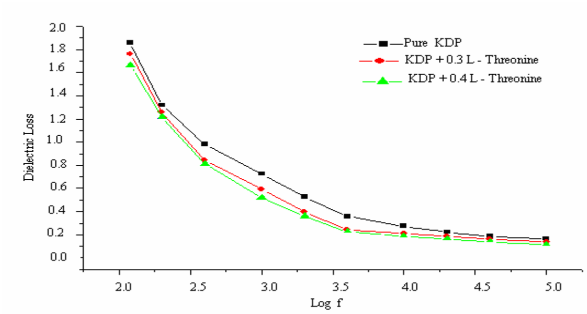


Fig. 6. Plots of dielectric loss versus frequency of pure and L – Threonine doped KDP crystals.

For the measurements of SHG efficiency, the output of Nd:YAG Quantum ray laser was obtained through the crystalline powder sample, a Q-switched, mode –locked Nd:YAG laser was used to generate about 2.7 mJ/ pulse at 1064 nm fundamental radiation. This laser device can be operated in two different modes. In the single shot mode, the laser emits an 8 ns pulse. While in the multi-shot mode, the laser produces a continuous train of 8 ns pulses at a repetition rate of 10 Hz. In the present study, a single shot mode of 8 ns laser pulse with a spot radius of 1 mm was used. This experimental set up used a mirror and 50/50 beam splitter to generate a beam with pulse energies of about 2.7 mJ. The input laser beam was allowed to pass through an IR reflector and then directed on the micro-crystalline powdered sample packed in a capillary tube of a diameter of 0.154 mm. The photodiode detector and oscilloscope arrangements measured the light emitted by the sample. Micro-crystalline powder of KDP or urea is taken in a similar capillary tube sealed at one end for comparison. The intensity of the second harmonic output from the sample is compared with that of KDP. In this manner the figure of merit of SHG of the sample is estimated [14]. For Nd: YAG laser the fundamental beam of 1064 nm generates the second harmonic signal of 532 nm. The output pulses were measured for different samples with reference to pure KDP (Pure KDP has out put 266 mV, this value is taken from sample available at ICPC , I.I. Sc., Bangalore) and the results are compiled in table 2.

Table. 2 Second harmonic efficiency for pure and L-threonine doped KDP crystal.

Sample	Second harmonic signal output in mV	Second Harmonic Generation Efficiency
Pure KDP Crystal	266	1
KDP + 0.3% L-Threonine	296	1.11
KDP + 0.4% L-Threonine	330	1.24

The effect of L– threonine doping on thermal stability of KDP crystal is studied by employing Thermo-gravimetric Analysis (TGA). Figurers 7 (a, b, c) indicate thermo-grams for pure KDP, 0.3 % L– threonine doped KDP and 0.4 % L– threonine doped KDP, respectively. It has been observed that for pure KDP crystals that initially crystal looses water of hydration at 201 ^{0} C and then becomes anhydrous at 336.718 ^{0}C and remains in that form up to the end of the analysis. For 0.3 wt % and 0.4 wt % L-threonine doped KDP crystals the dehydration process starts at 190.5 ^{0}C and crystals become anhydrous at 301^{0}C, respectively. The weight loss percentages are 12.85%, 13.22% and 13.47% for pure KDP and 0.3 % and 0.4% L-threonine doped KDP crystals, respectively. This suggests that on increasing doping of L- threonine the weight loss percentage increases indicating less crystalline stability. One can notice from the thermo-grams that on increasing the level of L– Threonine doping, the dehydration process starts early and the crystal becomes anhydrous faster than the pure KDP. Since amino acid becomes unstable at lower temperature, it weakens KDP crystal and as a result the dehydration process takes place early and faster as compared to pure KDP. This also proved that the amino acid has entered KDP crystal lattice in doped form.

The SGH efficiency of KDP crystal increases as concentration of L – Threonine increases. The earlier reports of doping of L-arginine in KDP [14] and L-Histidine, L- Glutamic acid and L-valine doping in KDP [15] have also given encouraging results by exhibiting increase in the SHG efficiency. The doping of L-Threonine in KDP is also as promising as the doping of other amino acids.

The use of thermogravimetry data to evaluate the kinetic parameters of solid state reaction involving weight loss has been investigated by many workers [30-32]. Very often the pyrolysis occurs through a many-stepped mechanism. The shape of the curve is determined by the kinetic parameters of pyrolysis such as order of reaction, frequency factor and energy of activation. The kinetic parameters of dehydration process of pure and L–Threonine doped KDP crystals were evaluated by using the Coats and Redfern [30] relation, which has been discussed in detail elsewhere [14,31,32]

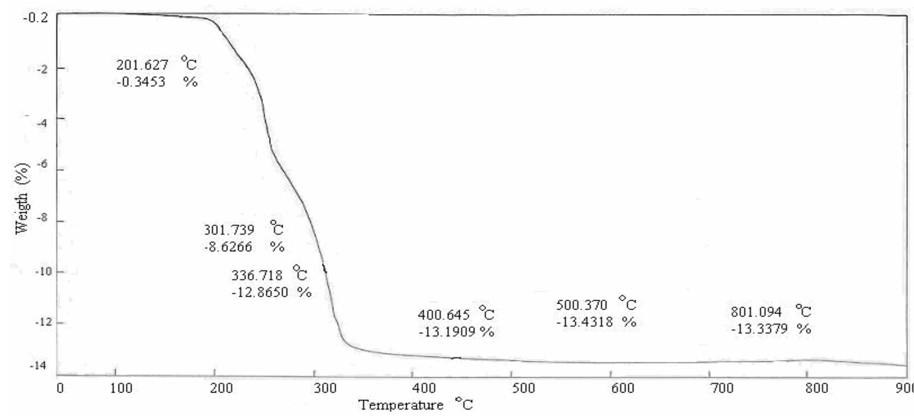


Fig.7. (a) Thermogram of pure KDP crystal

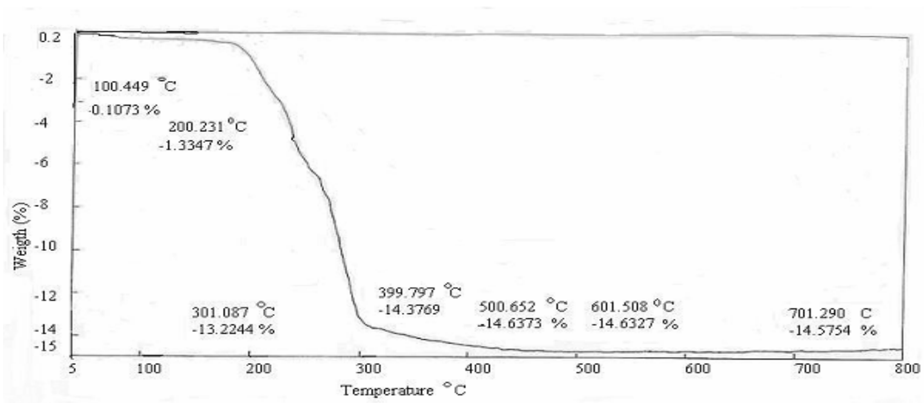


Fig. 7 (b). Thermogram of 0.3% L – Threonine doped KDP crystal .

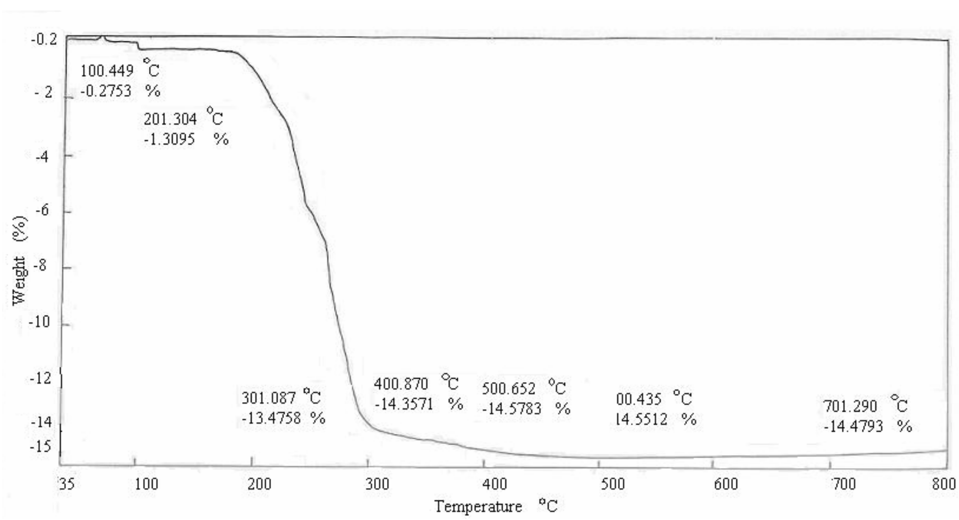


Fig. 7. (c) Thermogram of 0.4% L – Threonine doped KDP crystal.

Table 3 compiles the values kinetic and thermodynamic parameters of pure and amino acid doped KDP crystals. The values of activation energy and frequency factor decrease as the amount of L- threonine doping increases. The activation energy is considered as a barrier to be surmounted for reactants to combine to form the product. Hence the higher value of activation energy for pure KDP crystal indicates more stable nature. This can be verified from the thermograms also.

Table 3. Kinetic and thermodynamic parameters for pure and L-threonine doped KDP crystal.

Sample	Order of reaction	Frequency factor	$\Delta^{\#}S^{0}$ $JK^{-1}mol^{-1}$	$\Delta^{\#}H^{0}$ kJ mol^{-1}	$\Delta^{\#}G^{0}$ kJ mol^{-1}	Activation energy kJ/mol
Pure KDP Crystal	½	3.24×10^{21}	162.25	95.25	11.59	105.82
KDP + 0.3% L-Threonine	0	3.2×10^{20}	126	69.87	8.76	89.53
KDP + 0.4% L-Threonine	3/4	3.2×10^{16}	67	58.72	22.71	67.25

The thermodynamic parameters such as the standard entropy of activation, $\Delta^{\#}S^{0}$, standard enthalpy of activation, $\Delta^{\#}H^{0}$, and standard Gibbs free energy of activation, $\Delta^{\#}G^{0}$, have been estimated by using standard formulae for dehydration of pure and doped KDP crystals[14,31,32].

The thermodynamic parameters are given in table 3. It can be noted that on increasing the doping of L- Threonine in KDP, the value of standard entropy and standard enthalpy decreases. The single crystalline nature of the sample is the most ordered form of the sample and the dehydration of the sample brings the disorder in the sample, therefore, the large $\Delta^{\#}S^{o}$ is observed obviously in the case of pure KDP crystals than in the doped crystals.

Looking at various characterization results the doping of L threonine in different amount in KDP crystals improves SHG efficiency, increase optical transparency, dielectric property. The UV cut off limit is not getting changed contrary to this the thermal stability of the crystals becomes poor on increasing doping of L-threonine. The doping of L-threonine in KDP crystals improves its properties for NLO applications.

4. Conclusions

Pure and L- Threonine doped KDP crystals were grown by slow evaporation technique. FT–IR spectra, C H N analysis and paper chromatography confirmed the presence of amino acid, L- Threonine, in KDP crystals. Thermo-grams of pure and L- Threonine doped KDP suggested that as the doping increases the crystals become thermally less stable and dehydrate faster at comparatively lower temperature. The values of kinetic and thermodynamic parameters decreased as the amount of doping increased in crystals. The higher values of activation energy and standard entropy of activation suggested more stable condition for pure KDP than L-Threonine doped KDP. The doping of L- Threonine made the crystals comparatively more thermally unstable. The dielectric study suggested that the doping of L-threonine decreased the values of dielectric constants. The doping of L – Threonine decreased the space charge polarization and also the dielectric loss in comparison to pure KDP. As the doping of L- Threonine increased the SHG efficiency and the percentage transparency increased, however, the UV cut off remained unchanged. The doping of L-threonine is advantageous for the NLO application point of view.

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