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Research Paper

Growth and Elemental, FTIR Spectroscopic, Thermal and UV-Vis Studies of Pure and Alanine Doped Lithium Dihydrogen Phosphate Crystals

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Abstract— Pure and different weight% alanine doped lithium dihydrogen phosphate (LDP) crystals were grown at room temperature by the solution growth technique. The EDAX analysis showed the presence of the atoms of alanine molecule in the crystalline lattice of pure LDP, the weight% of which was observed to rise with increase in weight % of the alanine, which confirmed the successful doping of the alanine in the crystal lattice of pure LDP crystal. The FTIR spectra showed the presence of all the necessary functional groups of LDP in pure as well as in alanine doped LDP crystals. No significant effect of alanine doping on the crystal structure of pure LDP was observed. The thermal analysis of pure and different wt% alanine doped LDP crystals indicated the reduced thermal stability of alanine doped LDP crystals as well as shifting of thermal decomposition temperature of pure LDP towards higher temperature side, without affecting the weight loss of pure LDP. The UV-Vis transmittance profile of alanine doped LDP crystals showed shifting of cut-off wavelength towards lower wavelength side and reduction in the energy bandgap value. The results are discussed.

Keywords— Lithium dihydrogen phosphate (LDP) crystal, alanine, FTIR, UV- Vis, Thermal study

1. Introduction

The pure and doped crystals of various phosphate compounds like ADP, KDP and LDP are investigated by the various researchers in order to investigate the modifications in the various properties of the parent compound for basic research and practical applications [1-6]. It has been observed that ammonium dihydrogen phosphate and potassium dihydrogen phosphate are the widely studied phosphate compounds and large number of reports is available, while less investigation is reported on the pure and doped dihydrogen phosphate of lithium. Therefore, the present authors have aimed to investigate the properties modifications of pure LDP due to the effect of dopant and due to the change in the weight% of dopant.

The alanine, which is an alpha amino acid, having expanded molecular formula CH3HCNH2COOH was chosen as dopant. It contains an amine (NH2) group and a carboxylic acid (COOH) group, both attached to the central carbon atom which also carries a methyl (CH3) group side chain. The structure of LDP consists of tetrahedral groups of phosphate ion and LiO4, which are bonded together by oxygen ions [7]. In the Raman spectroscopic data of LDP, reported by R. Dekhili et al [7] within range of temperature 170 to 220 oC, intensity breakdown in the monotonous behavior with temperature with two anomalies around 176 oC and 210 oC temperature for all main Raman lines were reported. In the present case, the doping of alanine may reflect in terms of variation in intensity of the bond or in terms of presence of some additional characteristic vibrations of alanine. Further, the doping of alanine is also expected in terms of variation in the thermal stability as well as in decomposition temperature of pure LDP with change in weight% of the residual product. Optical data of LDP are not available in the literature. Therefore, the present study is also aimed to study the effect of dopant on some optical characteristics of pure LDP.

2. Experimental Technique

The crystals of pure LDP and 0.3wt%, 0.6wt% and 0.9wt% alanine doped LDP were grown at room temperature by the solution growth technique. First, 100 ml saturate solution of pure LDP was prepared by dissolving required amount of LDP powder. Then in the other three beakers again 100 ml saturate solution of pure LDP was prepared and then in each beaker, 0.3gm, 0.6gm and 0.9gm alanine was added and dissolved. In this way, four beakers were prepared with saturate solution of pure LDP and alanine added solution of LDP. All the solutions were stirred well for 3 hours and then filtered in other beakers. The beakers were covered with filter paper, having some pin halls for the process of evaporation.

The beakers were placed where there was a dust free environment without disturbance. After about 25 days, good quality, transparent, colorless crystals and having flower shaped morphology crystals were observed in each beaker. The grown crystals were harvested, washed with distilled water and after drying, photographs were taken by placing the crystals on the graph paper, which are shown in the figure 1.

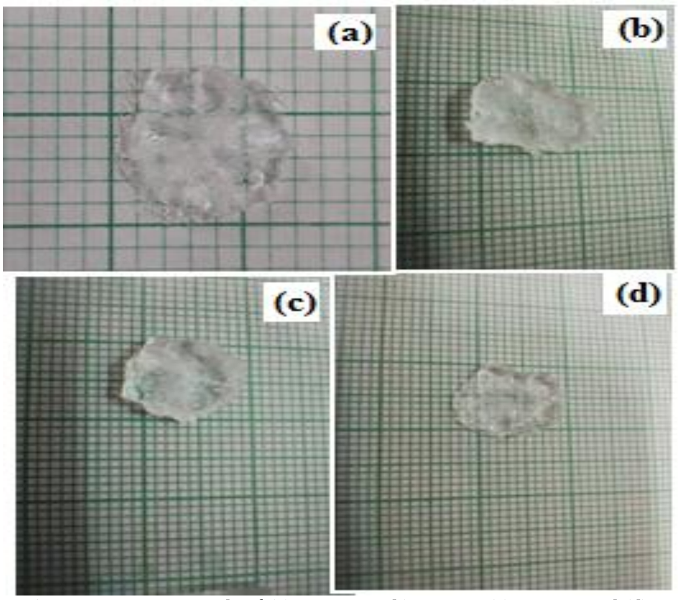

Figure 1: Grown crystals of (a) pure LDP (b) 0.3wt% (c) 0.6wt% and (d) 0.9wt% alanine doped LDP

All the crystals were characterized by various analyses. EDAX analysis was carried out by using the Philips XL-30 instrument set up in order to find the presence of the atoms of the dopant alanine molecule. Fourier Transform Infra-Red (FTIR) analysis is carried out on Thermo Nicolet Avtar 370 set up within the frequency range 4000cm^{-1} to 400cm^{-1} in KBr medium in order to identify the presence of characteristic vibrations of phosphate and LiO_4 and the effect the dopant alanine molecule on the characteristic vibrations of phosphate. The thermal analysis was carried out on Perkin Elmer STA-8000 set up from room temperature to 700^{o}C at heating rate 15^{o}C/min in the air atmosphere in order to find out the presence of various decomposition stages of pure LDP and the effect of doping of alanine in different weight% on various decomposition stages of LDP. The transmittance of UV-Vis data were recorded on Shimadzu UV-1700 Phamaspec by adopting dissolution method having HPLC grade water as internal standard. The maximum transmission and absorbance (in %) was measured by injecting the samples directly into UV spectrometer. Obtained UV chromatogram was recorded by Shimadzu UV prob 2.6 software.

3. Result and Discussion

3.1 EDAX analysis: The EDAX study was carried out to find out the weight% of the atoms of pure LDP and alanine doped LDP. Table 1 shows the wt% of different atoms from EDAX, which are present in the grown crystals of pure and alanine doped LDP.

Table 1: EDAX Result

Sample Name	Carbon (C) Wt%	Nitrogen (N) Wt%	Oxygen (O) Wt%	Phosphorous (P) Wt%
Pure LDP	-----	-----	64.00	35.00
0.3wt% alanine doped LDP	12.78	5.17	54.06	19.95
0.6wt% alanine doped LDP	14.97	5.72	55.62	23.69
0.9wt% alanine doped LDP	18.72	7.27	55.02	27.03

The chemical formula of LDP is LiH_2PO_4. Therefore, EDAX analysis of LDP shows the presence of both atoms, i.e., oxygen (O) and phosphorous (P). The chemical formula of alanine is $C_3H_7NO_2$. Therefore, the EDAX study of alanine doped LDP shows the presence of carbon (C) and nitrogen (N), along with oxygen (O) and phosphorous (P) of pure LDP. Further, the increased weight% of alanine shows the increased weight% of carbon and nitrogen, which confirms the successful doping of alanine in the LDP crystal. Note that the addition of alanine in small quantity, i.e., 0.3gm, 0.6gm and 0.9gm in 100 ml of saturated solution of LDP, the difference in solubility and crystal growth rate of LDP and alanine may result into the limited amount of dopant that enters into lattice sites of LDP.

3.2 FTIR spectroscopy analysis: Figure 2 shows the FTIR spectra of pure and alanine doped LDP crystals and table 2 shows the observed absorption frequencies and their assignments in relation to their characteristic vibrational modes.

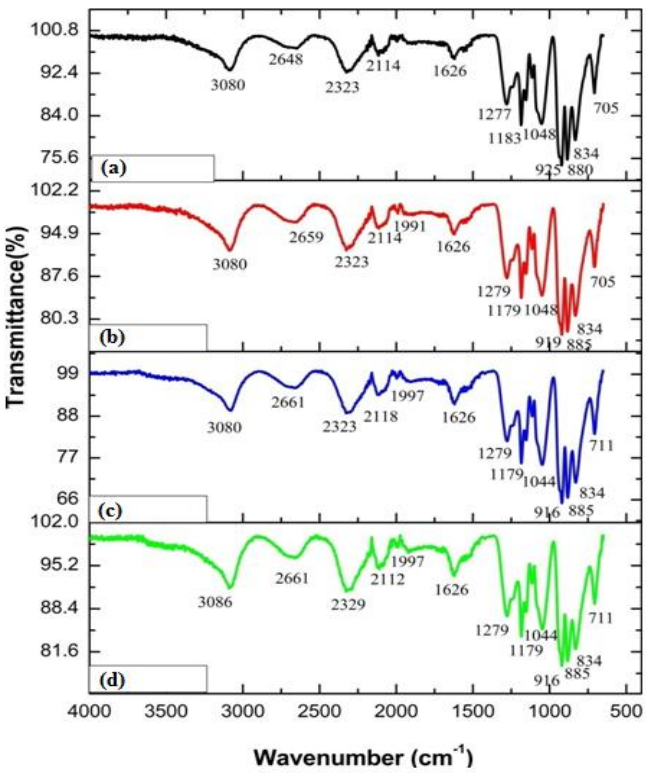

Figure 2: FTIR spectra of (a) Pure LDP (b to d) 0.3wt%, 0.6wt% and 0.9wt% alanine doped LDP

In the crystal of pure LDP, the absorption bands observed at 3080 cm^{-1} and at 2648, 2323, 2114 and 1626 cm^{-1}, can be attributed to the OH vibrations of intermediate and strong hydrogen bond, respectively [8]. As alanine is doped; the band observed at 3080 cm^{-1} is observed to shift slightly towards higher wavenumber, i.e., at 3086 cm^{-1} for the 0.9wt% alanine doped LDP crystal. The shifting of this band towards higher wavenumber indicates the reduced strength of the hydrogen bonding due to the presence of alanine. This may be the effect of the presence of hydroxy group of alanine, exist between neighboring molecules. The band observed at 1277 cm^{-1} in pure LDP can be attributed to the in-plane deformation vibration of OH [8]. In the alanine doped LDP, this vibration is observed to shift slightly towards higher wavenumber side and observed at 1279 cm^{-1}. The bands observed at 1183 and 1179 cm^{-1} and at 1048 and 1044 cm^{-1} in pure and alanine doped LDP crystals shows anti-symmetric stretching mode (ν_3) of PO_4 or out-of-plane bending vibrations of OH group [8]. A symmetric stretching mode (ν_1) of PO_4 is observed around 920 and 880 cm^{-1} in pure and alanine doped LDP crystals. The vibrations observed at 834 cm^{-1} and at 705 and 711 cm^{-1} can be ascribed to the overtone of PO_4 or LiO_4 [8]. The assignment of LiO_4 is based on the fact that the crystal structure of LDP is composed of LiO_4 and $H_2PO_4^{-1}$, which share oxygen atoms.

The FTIR analysis shows that there is no significant effect of alanine doping on the crystal structure of pure LDP is observed except reducing the strength of hydrogen bonding and the variation in the intensity of absorption bands. No additional characteristic vibrations of alanine such as CH vibrations of side chain CH_3 group, NH vibrations of NH_2 group, C = O vibrations of COOH group are observed in the alanine doped LDP crystals.

Table 2: Assignments of functional groups with frequency

Assignments	Wave numbers (cm^{-1}) Pure LDP Sample 1	0.3wt% alanine doped LDP Sample 2	0.6wt% alanine doped LDP Sample 3	0.9wt% alanine doped LDP Sample 4
O – H stretching vibrations of intermediate H bond	3080	3080	3080	3086
O – H stretching vibrations of strong H bond	2648, 2323, 2114, 1626	2659, 2323, 2114, 1626	2661, 2323, 2118, 1626	2661, 2329, 2112, 1626
O – H in-plane deformation vibration	1277	1279	1279	1279
Anti-symmetric stretching mode (ν_3) of PO_4 and/or out-of-plane bending vibrations of OH	1183, 1048	1179, 1048	1179, 1044	1179, 1044
symmetric stretching mode (ν_1) of PO_4	925, 880	919, 885	916, 885	916, 885
overtone of PO_4 or LiO_4	834, 705	834, 705	834, 711	834, 711

3.3 Thermal analysis: The curves of Thermogravimetry of pure and alanine doped LDP crystals are shown in the figure 3, while the remaining weight loss% are given in the table 3.

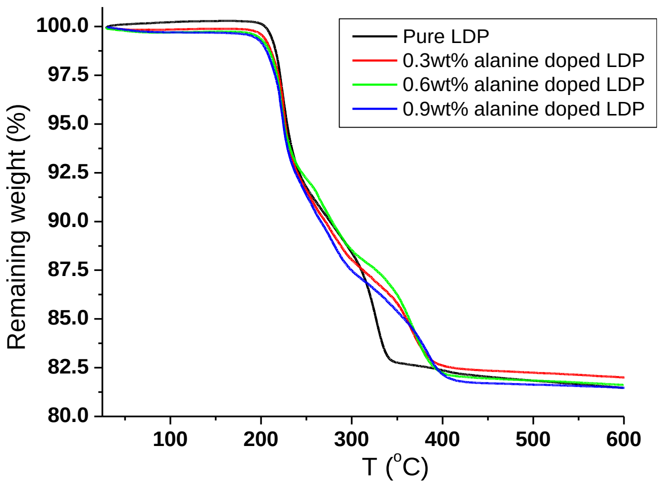

Figure 3: TG curves of pure and alanine doped LDP crystals

From the figure 3, it is observed that starting from the room temperature, pure LDP crystal shows plateau region up to 200 °C, which indicates the thermal stability of pure LDP crystal up to 200 °C. After the plateau, pure LDP loses 18% weight within range of temperature 200 to 345 °C. This weight loss belongs to the conversion of LDP into $LiPO_3$. After this first stage of decomposition, the product $LiPO_3$ remains stable up to the upper limit of temperature 600 °C. This process of thermal decomposition of pure LDP is in good agreement with the report [9].

The effect of doping of alanine on the thermal property of pure LDP is observed in terms of stability of LDP, variation in decomposition rate of LDP and shifting of temperature of decomposition of LDP. First, 0.3wt%, 0.6wt% and 0.9wt% alanine doped LDP crystals show the thermal stability up to the temperature limit 188 °C, 186 °C and 181 °C, respectively. It indicates that the thermal stability reduces as the alanine is doped and as its weight% increases. Then 0.3wt%, 0.6wt% and 0.9wt% alanine doped LDP crystals follow the decomposition process almost similar to that of pure LDP up to the temperature 302 °C, 310 °C and 316 °C, respectively. Within 305 °C to 345 °C, pure LDP crystal shows rapid decomposition, while 0.3wt%, 0.6wt% and 0.9wt% alanine doped LDP crystals show the decomposition process within temperature range 302 to 396 °C, 310 to 398 °C and 316 to 413 °C with reduced rate. Hence, the presence of alanine reduces the decomposition rate of pure LDP crystal and shifts the temperature of thermal decomposition of LDP into $LiPO_3$ towards higher temperature side. The weight of the residual product remains same in pure as well as in alanine doped LDP crystals. It means, the presence of alanine prevents the thermal decomposition of pure LDP at lower temperature, i.e., at 345 °C and shifts towards higher temperature, i.e., at 396 °C, 398 °C and 413 °C for 0.3wt%, 0.6wt% and 0.9wt% alanine doped LDP crystals. The increase in the temperature region of decomposition of pure LDP into $LiPO_3$ can be attributed to the increase in bond energy due to the presence of dopant alanine.

Table 3: Thermogram result

Sample	Temperature range (°C)	Remaining weight (%)
Pure LDP	From RT to 200	100
	From 200 to 345	82
	From 345 to 600	82
0.3wt% alanine doped LDP	From RT to 188	100
	From 188 to 396	82
	From 396 to 600	82
0.6wt% alanine doped LDP	From RT to 186	100
	From 186 to 398	82
	From 398 to 600	82
0.9wt% alanine doped LDP	From RT to 181	100
	From 181 to 413	82
	From 413 to 600	82

The DSC curves of pure and different wt% alanine doped LDP crystals are shown in the figure 4.

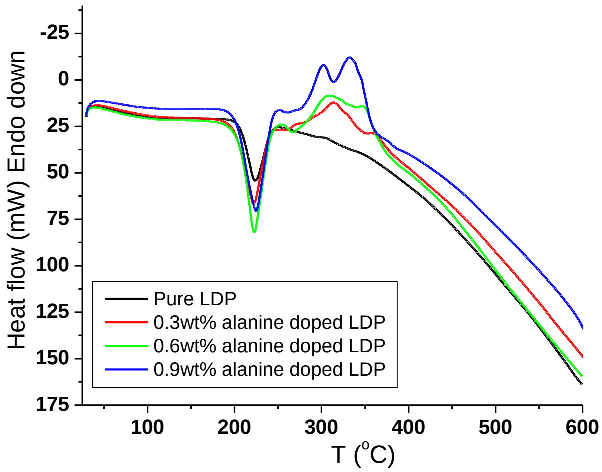

Figure 4: DSC curves of pure and alanine doped LDP crystals

The DSC curve of pure LDP crystal shows an endothermic peak having onset and peak temperatures of 200 °C and 225 °C, respectively. This is in agreement with the result of the previous reports [9,10]. This endotherm corresponds to the intermediate product. As alanine is doped, the peak temperatures are observed to vary slightly. 0.3 wt%, 0.6wt% and 0.9wt% alanine doped LDP crystals show 222 °C and 224 °C peak temperatures. It indicates that the temperature of the formation of intermediate product decreases slightly. All the peaks possess good sharpness indicating good crystallinity of the grown crystals. Further, 0.6wt% and 0.9wt% alanine doped LDP crystals show one more endothermic peak at temperature 266 °C and 314 °C, respectively. These peaks can be attributed to the second intermediate product of LDP, before its conversion into lithium metaphosphate ($LiPO_3$). The intermediate products may be $Li_5H_4P_5O_{17}$, $Li_3H_2P_3O_{10}$ or $Li_4H_2P_4O_{13}$ [9].

Figure 5 shows the DTG curves of pure and different wt% alanine doped LDP crystals.

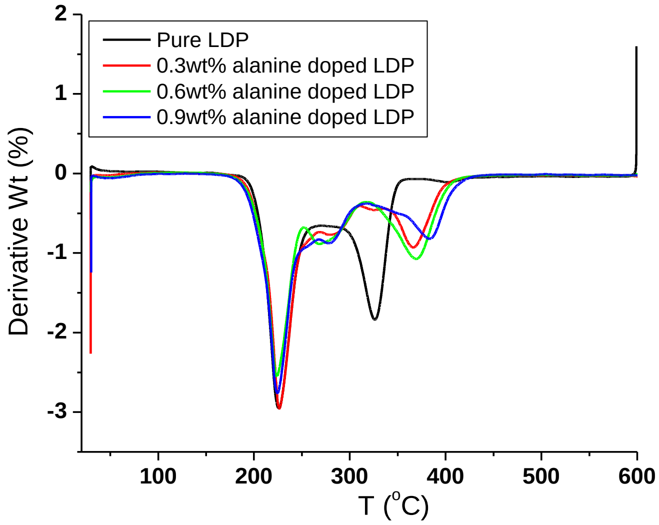

Figure 5: Derivative curves of pure and alanine doped LDP crystals

It is observed from the DTG curves that pure as well as alanine doped LDP crystals show two peaks, which corresponds to the endothermic peak of the intermediate product as well as mass loss associated for the conversion of the intermediate product into $LiPO_3$, respectively. The TG curves show two humps accordingly. It is observed that DSC, TGA and DTG curves are closely related.

For the pure LDP, the DTG onset and peak temperatures of the first peak are 200 and 225 °C, respectively. The weight loss started at 200 °C in DTG curve is due to the onset of the thermal decomposition. Thus, coincidence between the DSC (200 and 225 °C) and DTG (200 and 225 °C) onset and peak temperatures of the first thermal event should be a consequence of structural phase transition and the same is supported by the single well defined endothermic peak, without showing the presence of a sequence of very small DSC endothermic anomalies.

The second DTG peak observed in the case of pure LDP crystal can be attributed to the mass loss during the conversion of intermediate product into $LiPO_3$. When alanine is doped, the peaks are observed to shift towards higher temperature side with reduction in the decomposition rate at peak temperature. These results are in agreement with the TG results, which show increase in the weight loss temperature. The second DTG peak offset temperature is 350 °C of pure LDP crystal, which corresponds to the weight loss of 18%. As alanine is doped, the second DTG peak offset temperatures are observed at 396 °C, 398 °C and 413 °C temperature, which correspond to 18% weight loss.

3.4 UV-Vis spectroscopy analysis

Figure 6 shows the variation in % of transmittance with wavelength of pure and alanine doped LDP crystals.

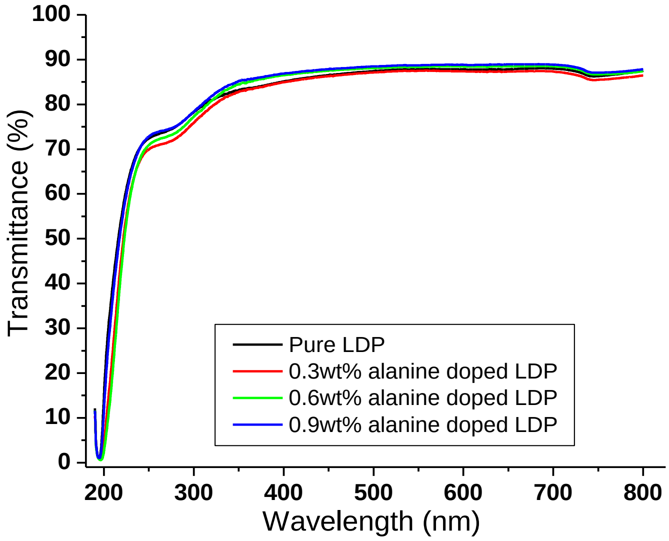

Figure 6: UV-Vis transmittance profile

Pure LDP crystal shows cut off wavelength of 194 nm and then shows increase in % of transmittance up to 87%. As alanine is doped, the cut off wavelength is observed to shift towards lower wavelength side, i.e., at wavelength 194 nm and the % of transmittance are observed up to 89%. Hence, the effect of alanine is observed in terms of shifting of lower cut-off wavelength towards lower wavelength side with increase in % of transmittance. These profile of pure and alanine doped LDP crystals is a desirable profile for the application of the grown crystals as a fabricating material for photonics and optoelectronic devices.

Tauc's method [11] is used for the measurement of optical bandgap of pure and alanine doped LDP crystals by using a relation: $\alpha h\nu = A(h\nu - E_g)^n$,
Where, the symbols have the meaning as reported in the literature [3].

For the determination of the direct optical energy bandgap of pure and alanine doped LDP crystals, $(\alpha h\nu)^2$ dependence on photon energy (hν), as shown in the figure 7 is used.

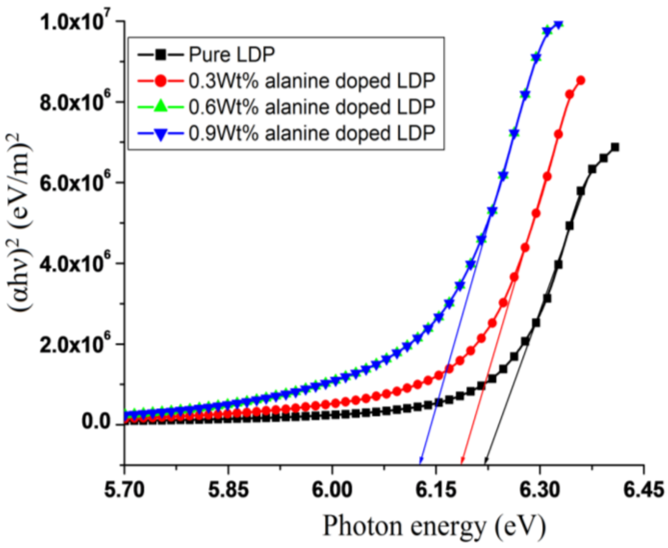

Figure 7: Tauc's plot

As shown in the figure 7, the straight line is extrapolated on the x-axis, which gives the value of the direct optical energy bandgap of all the grown crystals. Pure LDP crystal shows the value of bandgap 6.221 eV, while 0.3wt%, 0.6wt% and 0.9wt% alanine doped LDP crystals show 6.188 eV, 6.128 eV and 6.128 eV, respectively optical bandgap values. The result indicates that the doping of alanine reduces the value of optical energy bandgap, which may be due to the formation of vacancies in the crystal lattice of pure LDP due to the charge compensation effect and the shifting of the optical band edges towards lower wavelength, i.e., higher hν side compared to pure LDP.

4. Conclusion: Pure and alanine doped LDP crystals are grown at room temperature by the solution growth method. The EDAX analysis confirms the presence of dopant alanine atoms, the weight% of which increases with increase in weight% of alanine and hence, confirms the successful doping of alanine in the crystal lattice of pure LDP. FTIR spectroscopic analysis shows the presence of characteristic vibrations of phosphate group in pure and isoleucine doped LDP crystals. The effect of doping is observed in terms of the variation in the intensity of absorption bands. The thermal analysis shows that alanine shifts the thermal decomposition temperature of pure LDP towards high temperature side without affecting the weight% of the residual product. The DSC curve shows endothermic peak corresponding to the intermediate product. The derivative curve shows two peaks corresponding to the endothermic peak of the intermediate product and mass loss associated with the conversion of the intermediate product into $LiPO_3$, respectively. The transmittance profile of alanine doped LDP shows increase in % of transmittance and shifting of cut off wavelength towards lower wavelength side. Alanine doped LDP crystals show reduced value of energy bandgap.

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Conflict of Interest: The authors declare that there are no competing interests.

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Authors contribution: Experimental, conceptual study and data collection: Hepi Ladani, V. J. Pandya and Radhika Rathod; Analysis and Interpretation of Results: Hepi Ladani and Prof. H. O. Jethva; Draft manuscript design: Hepi Ladani; Supervising and editing manuscript: Prof. H. O. Jethva.

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