

FT-IR, Thermal and NLO Studies on Amino Acid (L-Arginine and L-Alanine) Doped KDP Crystals

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Single crystals of pure and amino acid (L-arginine and L-alanine) doped potassium dihydrogen phosphate (KDP) for second harmonic generation have been grown from low temperature solution growth method by employing slow evaporation of the solvent. FT-IR spectrum of pure and doped KDP crystals confirms qualitatively the doping of the L-arginine and L-alanine in the host crystals. UV-visible spectroscopy shows the improvement in the transparency. Crystal structure has been studied by powder X-ray diffraction. Modification in the lattice parameters has been observed. Improvement in the SHG efficiency was studied by the Kurtz and Perry method. Thermal analysis has been performed on the grown crystals.

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1. Introduction

The numerous applications of the nonlinear optical (NLO) crystals in the vast field of science and technology [1–6] made the process of search of the new NLO crystals and improvements in the properties of the known crystals a never stopping process. KDP crystal is widely used and thoroughly studied NLO crystal. Many researchers have tried to modify the properties and growth rate of the KDP crystal by either changing the growth conditions or by adding different impurities. The NLO and other properties of the crystal have been improved by doping of organic impurities [7–34]. The KDP crystal has been grown with high growth rate as much as 50 cm per day [35].

Kumaresan et al. [36] have grown the amino acids such as L-glutamic acid, L-histidine and L-valine doped KDP crystals. They found improved NLO properties of the KDP crystal, modifications in the structure, optical, mechanical, and electrical properties, too. Parikh et al. [37] and Kumaresan et al. [38] have studied L-arginine doped KDP crystal. They have investigated the effect of the doping on the NLO, thermal, mechanical properties and optical transparencies. In the present work, the dopant level of L-arginine in KDP has been optimized for the first time and it is found to be 4 mol%. No single reference has been observed for attempting the doping of L-alanine in KDP. In the present work, the growth of the L-arginine and L-alanine doped KDP crystals, its characterization and findings have been reported.

2. Experimental

2.1. Solubility study

It is desirable to study the solubility of the material in a suitable solvent before proceeding for the crystal growth. Solubility must be moderate and should have positive temperature gradient in a selected solvent. Solubility of the pure and doped KDP in water was studied gravimetrically. The solutions of pure and doped KDP were prepared separately and kept in a constant temperature bath for two hours with constant stirring. 50 ml solution of each sample was taken and dried in oven to measure the dissolved solute. Same process was repeated for different temperature. The slight change in the solubility has been observed for doped KDP as compared to the pure KDP in water. Further, the solubility has positive gradient with temperature. Thus the double distilled water was used as a solvent throughout the experiment. Solubility curves of the pure and L-arginine and L-alanine doped KDP crystals have been shown in Figs. 1 and 2.

2.2. Crystal growth

The pure and doped KDP single crystals were grown by dissolving purified KDP, L-arginine and L-alanine powders in appropriate amount in double distilled water and heated at a constant temperature 43 °C with continuous stirring using magnetic stirrer for two hours to form a mother solution. The solution is then filtered using the Whatmann filter papers and kept in optically heated constant temperature bath of an accuracy ± 0.01 °C at a temperature 40 °C to harvest the seed crystals within 2–3 days. The same process was used to prepare the solutions for the bulk crystal growth. Good quality seed crystals were used to grow the single crystals of bigger size within

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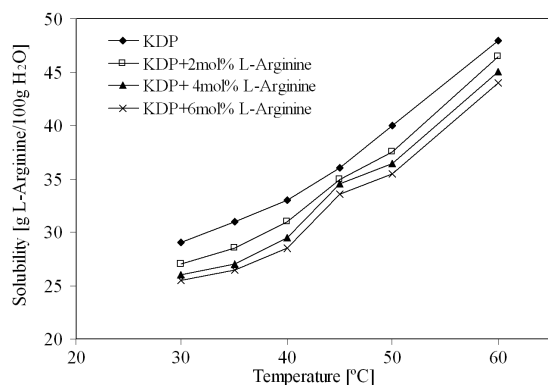


Fig. 1. Solubility curve of pure and L-arginine doped KDP.

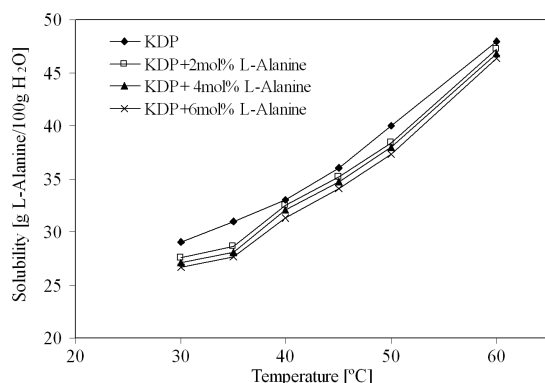


Fig. 2. Solubility curve of pure and L-alanine doped KDP.

10–15 days. In the experiment analytical reagent (AR) grade powders were used and further purified by repeated recrystallisation.

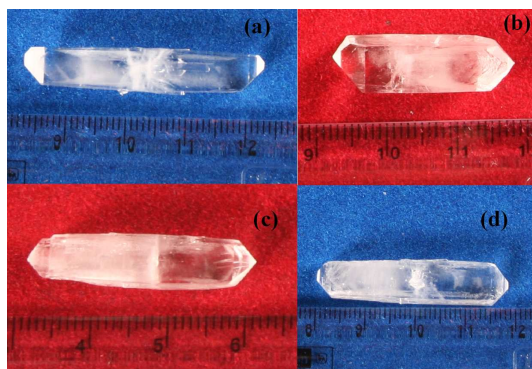


Fig. 3. Photographs of (a) 2 mol% L-arginine, (b) 6 mol% L-arginine, (c) 4 mol% L-alanine and (d) 6 mol% L-alanine doped KDP crystals.

Pure KDP crystal of size $38 \times 6 \times 5 \text{ mm}^3$ having good optical quality was grown within 10 days by dissolving purified KDP in double distilled water. The 2 mol%,

4 mol% and 6 mol% L-arginine doped KDP seed crystals and single crystals were independently grown by dissolving 2 mol%, 4 mol% and 6 mol% L-arginine and KDP powders in double distilled water separately. The pH of the solution was ranged from 4.2 to 4.4. The single crystals of 2 mol%, 4 mol% and 6 mol% L-arginine doped KDP of sizes $40 \times 6 \times 5 \text{ mm}^3$, $30 \times 7 \times 6 \text{ mm}^3$ and $33 \times 7 \times 6 \text{ mm}^3$ were grown within 10–15 days, respectively. The same process was used to grow the 2 mol%, 4 mol% and 6 mol% L-alanine doped KDP crystals of sizes $32 \times 10 \times 6 \text{ mm}^3$, $32 \times 7 \times 5 \text{ mm}^3$ and $38 \times 9 \times 6 \text{ mm}^3$, respectively. In this case, the pH of the solution was ranged from 4.3 to 4.5. The photographs of some of the grown crystals have been shown in Fig. 3.

2.3. Characterization

The grown crystals were subjected to the Fourier transform infrared (FT-IR) study to verify the doping of the amino acid: L-arginine and L-alanine in KDP crystals. X-ray diffraction (XRD) study was done to determine the crystal structures. Second harmonic generation (SHG) efficiency study was performed to measure the SHG efficiency of the grown crystals and thermal stability of the grown crystal was studied from thermal gravimetric analysis (TGA).

3. Results and discussion

3.1. Morphology

From the external observations of the pure and doped KDP crystals, it is clear that there is no change in the external morphology of the doped KDP crystals. During the crystal growth process continuous observations were taken in respect of growth rate over whole period of the growth. No detectable change in the growth rate of the doped crystals has been observed with reference to the pure KDP.

3.2. SHG efficiency measurement

The grown crystals were subjected to the NLO study to measure the SHG efficiency with respect to the pure KDP. To characterize the crystals, Kurtz and Perry method [39] was employed. In this experiment Q-switched, mode locked Nd:YAG laser of wavelength 1064 nm having pulse energy 2.35 mJ, pulse duration 8 ns and repetition rate 10 Hz was used. The output was measured at 532 nm wavelength. The observed data has been tabulated in Table I.

The SHG efficiency found to be increased with the concentration of the L-arginine. The remarkable change in the SHG efficiency has been reported up to 4 mol% doping of the L-arginine in KDP, which is in agreement with the results stated in Ref. [37]. For 6 mol% doping remarkable increase in the SHG efficiency has not been observed. Also in the L-alanine doped KDP crystals, the SHG efficiency found to be increased with the concentration. The maximum SHG efficiency 1.67 has been reported for both

TABLE III

FT-IR peak assignments [40, 41].

Pure KDP [cm ⁻¹]	2 mol%	4 mol%	6 mol%	Assignments
	L-arginine doped KDP [cm ⁻¹]			
3734.1, 2365.12	3426.47, 2998.57, 2777.71, 2491.76	2983.21, 2946.58, 2873.38, 2768.72, 2425.68	3610.57, 2925.55, 2852.71, 2427.56	P-OH stretching of H ₂ PO ₄ , O-H stretching of COOH and water of crystallization, N-H stretching of NH ₃ , C-H stretching of CH ₂ and CH
1750.24	1784.58	1707.08	1699.60	C=O stretching, P-O-H bending and -C=NH ₄ stretching
1279.19	1299.44	1300.8	1300.23	CH ₂ bending, P=O stretching of KDP
915.20	1099.66, 902.21, 877.70, 785.97, 647.80	1110.22, 900.19, 780.81	1104.77, 896.98	P-OH and C-H stretching P-OH deformation

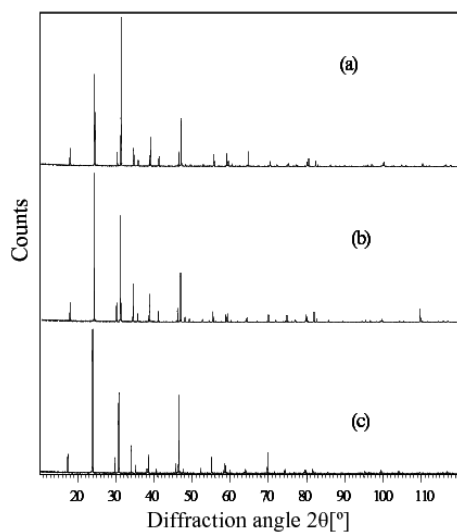


Fig. 5. Powder XRD Pattern of (a) pure, (b) 6 mol% L-arginine and (c) 4 mol% L-alanine doped KDP crystals.

The pure and L-arginine doped KDP crystals show a good transparency between 200 nm to 900 nm. As expected, the transparency increases with the concentration of the L-arginine. For 4 mol% L-arginine doped KDP crystal, significant increase in transparency has been observed. For 6 mol% L-arginine doped KDP crystal there is no considerable increase in the transparency with respect to 4 mol% L-arginine doping. It is also found that the lower wavelength cut-off shifts somewhat toward longer wavelength. For pure KDP, the cut-off has been observed at 200 nm but for 4 mol% and 6 mol% doped KDP crystal it shows at 205 nm.

For the L-alanine doped KDP crystals, the maximum transparency found to be for the 2 mol% L-alanine doped KDP crystal. For 4 mol% and 6 mol% L-alanine doped KDP crystals the transparency is improved but not as much as that for 2 mol% doped crystal. The effect of the doping on the lower wavelength cut-off has not been observed but doped crystals show sharp cut-off at 200 nm as compared to pure KDP.

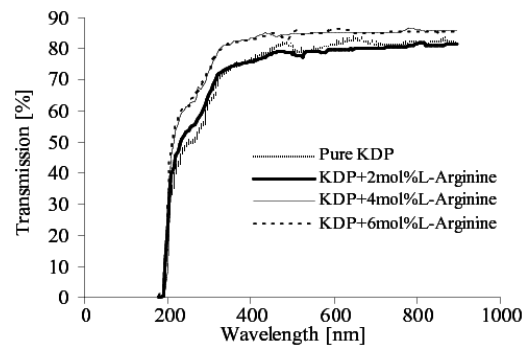


Fig. 6. UV-VIS-NIR spectra of pure and L-arginine doped KDP crystal.

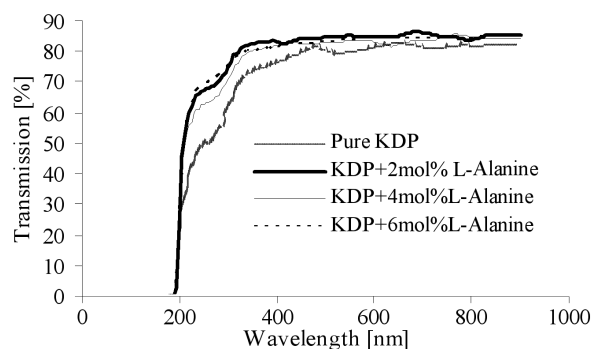


Fig. 7. UV-VIS-NIR spectra of pure and L-alanine doped KDP crystal.

3.6. Thermal analysis

The TGA curve of L-arginine and L-alanine doped and pure KDP crystals have been recorded on Perkin Elmer Dimmer TGDTA at a heating rate of 15 °C/min under argon atmosphere. For pure KDP crystal, after temperature about 230 °C the weight loss starts due to the liberation of volatile substances, probably water molecule of decomposed KDP (Fig. 8) [37].

The TGA curve for 6 mol% L-arginine doped KDP crystal has been shown in Fig. 9. The experimental results show that the initial weight loss starts at about

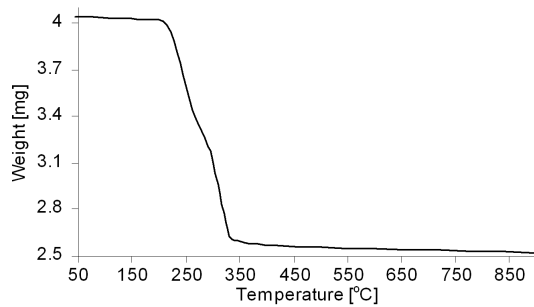


Fig. 8. TGA curve of pure KDP crystal.

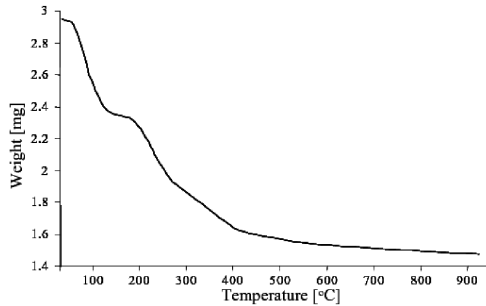


Fig. 9. TGA curve of 6 mol% L-arginine doped KDP crystal.

68°C and ends at 120°C with about 18% weight loss, which corresponds to the liberation of ammonia and water molecule. Second weight loss starts at about 204°C. Rapid weight loss occurs up to 263°C and continues slowly up to 400°C, which is possibly due to the decomposition of the KDP and remaining L-arginine.

The TGA curve of 4 mol% L-alanine doped KDP crystal (Fig. 10) shows the maximum weight loss in the temperature range 205–365°C. This is probably due to the decomposition of the KDP and L-alanine. Prolonged heating up to 900°C does not produce any weight loss.

This study confirms the decrease in the thermal stability of KDP crystals with increasing doping level of L-arginine and L-alanine.

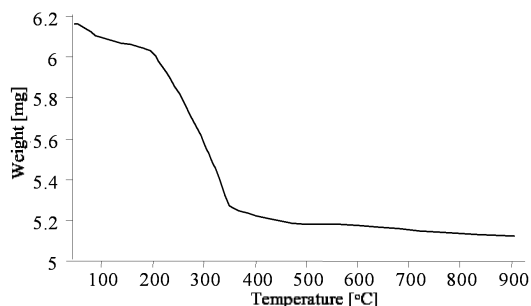


Fig. 10. TGA curve of 4 mol% L-alanine doped KDP crystal.

4. Conclusions

Pure and amino acid (L-arginine and L-alanine) doped KDP crystals were grown from solution at a temperature 40°C by employing slow evaporation of the solvent. An external observation of the doped crystals shows no change in the morphology of the doped crystals and also no change in the growth rate as compared to the growth rate of the pure KDP crystal.

FT-IR Spectroscopy of the pure and doped KDP crystals confirms the expected doping of the L-arginine and L-alanine in the doped KDP crystals.

Pure and doped KDP crystals crystallizes in the same tetragonal crystal system and the lattice parameters calculated from the XRD pattern of the pure and doped KDP crystals show very slight changes.

The increasing doping level in the KDP crystal improves optical transparency. A remarkable increase in optical transparency has been observed up to 4 mol% L-arginine doping. For 6 mol% doping, no substantial change is observed in comparison with respect to 4 mol% doping. In L-alanine doped crystals, the maximum transparency for 2 mol% doped KDP crystal has been reported.

SHG efficiency test confirms the increase in the SHG efficiency in doped KDP crystals. For 6 mol% L-arginine doped KDP crystal, the increase in the SHG efficiency with respect to 4 mol% doping is found to be negligible. In L-alanine doped crystals, SHG efficiency has been found the same for both 4 mol% and 6 mol% doping.

TGA study confirms that the stability of the crystal decreases with the increasing concentration of the L-arginine and L-alanine in KDP crystals.

Considering the changes in the optical transparency, SHG efficiency and Thermal stability 4 mol% L-arginine and 4 mol% L-alanine doping in KDP crystal is found to be more suitable for optimum properties for SHG applications. 4 mol% L-arginine and 4 mol% L-alanine doped KDP crystal may be used for SHG purpose with improved SHG efficiency and optical transparency at the place of pure KDP crystals.

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