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Effect of L-Arginine on the Growth of KDP Crystals

[1]N.Lavanya & [*2]B. Ravindran

[1]*Assistant Professor of physics, A.D.M college for Women Nagapattinam 611001 (India)*
[2]*Assistant Professor of Physics,Thiru.Vi.Ka.Govt.Arts College,Tiruvarur 610 003 (India)*

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[*]Corresponding Author
Email: ravitvk74[at]gmail.com

ABSTRACT

KDP doped with L - ARGININE single crystals have been grown by slow evaporation solution growth technique. The solubility data of KDP and L - ARGININE was first determined and the structure, optical, mechanical, properties of the crystals has been investigated. The crystalline perfection of the grown crystal is found to be estimated through X-ray diffraction analysis. FTIR confirms the presence of functional group and the optical transparency reveals to be enhanced much by the mixed crystals through UV-Vis-NIR studies.

1. Introduction

Non linear optical (NLO) materials find extensive opto electronic applications such as optical frequency conversion, optical data storage, optical switches etc., due to their second order NLO capability of high efficiency in frequency conversion from infrared or visible laser radiation to visible or ultraviolet wave lengths. Necessity of fabricating highly efficient NLO materials is arising to satisfy the future application [1-4]. KDP group of materials are widely used in frequency conversion due to their modest nonlinearities [5].Even though having high mechanical strength, high melting point and good degree of chemical inertness,Inorganic materials are very poor in optical nonlinearity. But the organic materials are optically more non linear than inorganic materials [6]. The search for effective NLO materials reveals that L-Arginine based crystals are effective with excellent optical, thermal and mechanical properties [7]. L-Arginine forms a number of crystals with organic and inorganic acids with good NLO properties [8-12]. In the present investigation KDP has been doped with L-Arginine, in order to improve its SHG efficiency so that it can be used as better alternative to pure KDP for opto electronics applications.

2. Experimental procedure

Table : 1 - Nucleation Kinetics

Solution 1	(7mol%KLAC)KDP and 7mol% L-Arginine	Dissolved in 20ml of distilled water
Solution 2	(13mol%KLAC)KDPand 13mol % L-Arginine	Dissolved in 23ml of distilled water
Solution 3	(19 mol %KLAC) KDP and 19 mol % L-Arginine	Dissolved in 29ml of distilled water
Solution 4	(23mol %KLAC) KDP and 23 mol % L-Arginine	Dissolved in 30ml of distilled water.

Amino acid (L-Arginine) doped KDP crystals are grown by solution growth technique. Slow evaporation method was employed to grow these crystals. The concentration of dopants in the mother solution in varied from 7%, 13%, 19% and 23mol%. The growth was carried out for more than 25days from the aqueous growth medium.

3. Characterization Studies

3.1 Photos of L-Ariginine Doped Crystals

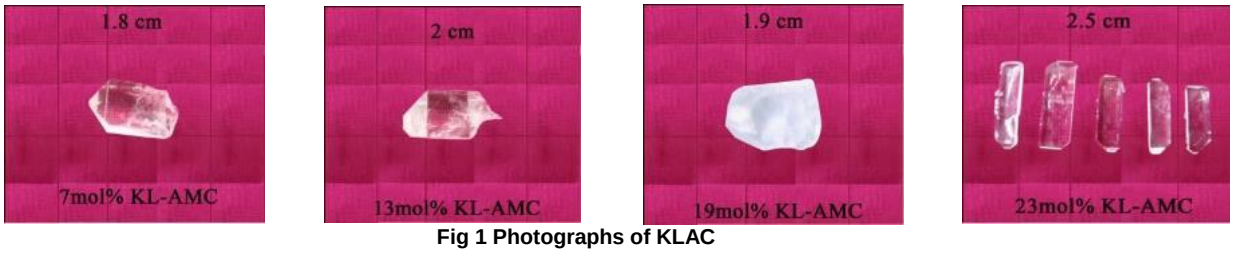


Fig 1 Photographs of KLAC

3.2 UV-Vis-NIR Spectroscopy

Optical transmission spectra were recorded for KDP-L-Arginine crystals in the wavelength region starting from 200 to 1100nm (Fig 2.1-2.2). It was found that the cut-off wave length changed due to L-Arginine dopant and absorption edge shifted to the higher wavelength side.

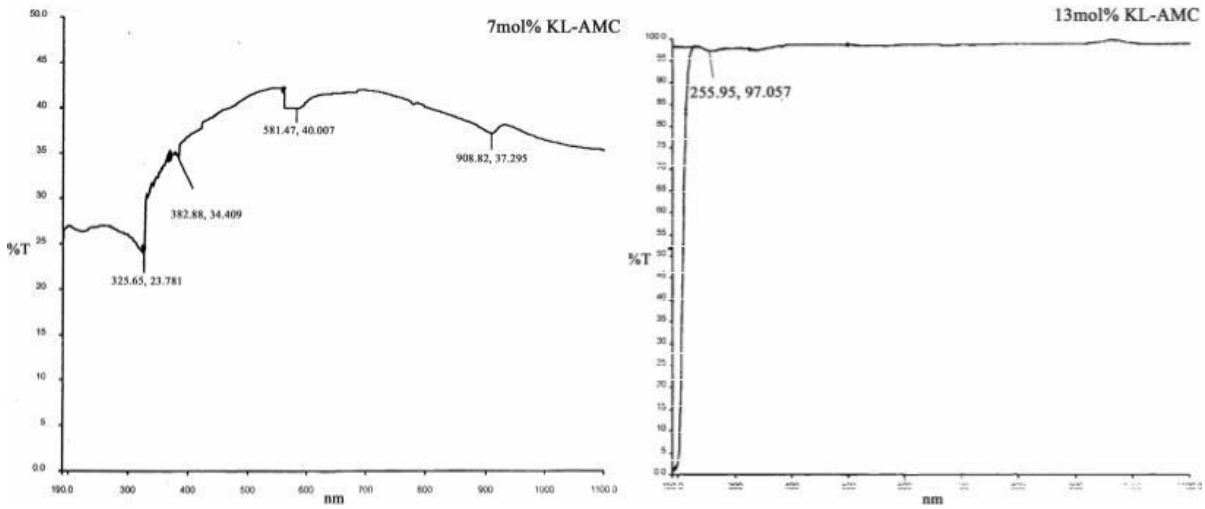


Fig. 2.1 UV –Vis Transmission Spectrum of 7mol % and 13mol% KLAC

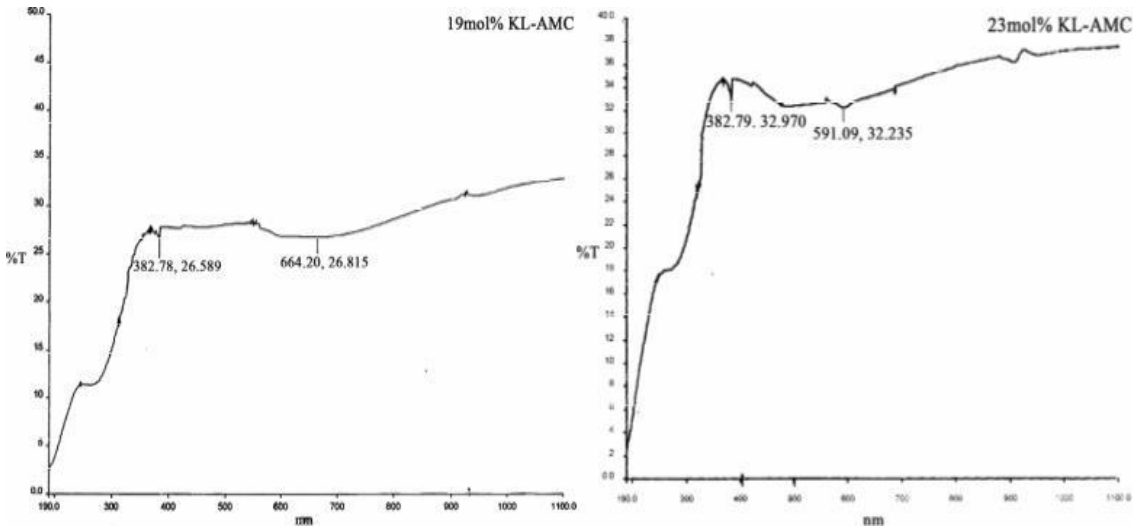


Fig 2.2 UV –Vis Transmission Spectrum of 19mol% and 23mol% KLAC

Table : 2 Calculated cutoff frequency of KLAC

System	Cut off wave length in nano meter	Percentage of transmittance
KDP7mol% L-A	370	35
KDP13mol% L-A	210	98
KDP19mol% L-A	350	28
KDP23mol% L-A	370	35

3.2.1. Energy Band Gap

Optical band gap was determined to be 2.8 ev, 3 ev, 3.6 ev respectively for different proportions of L-Arginine with KDP mixed crystals. It is shown in Fig (3.1-3.2)

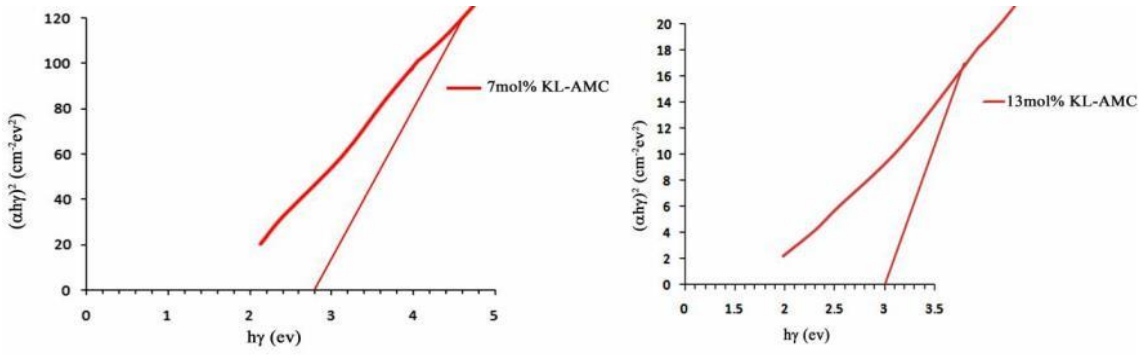


Fig 3.1 Band gap measurement of 7mol% and 13% KLAC

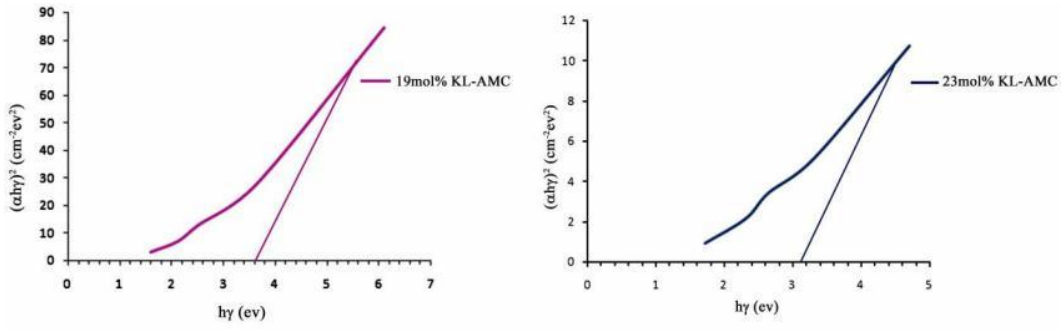


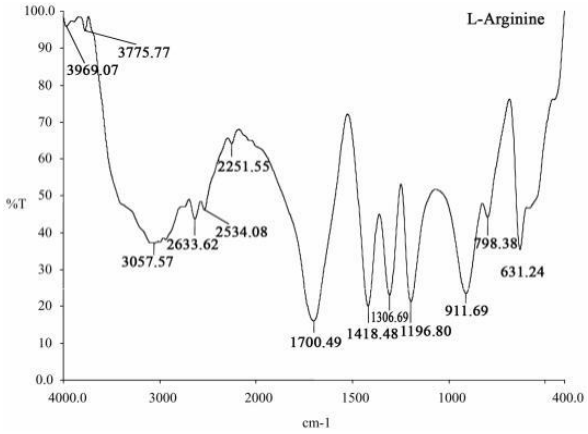
Fig 3.2 Band gap measurement of 19mol% and 23% KLAC

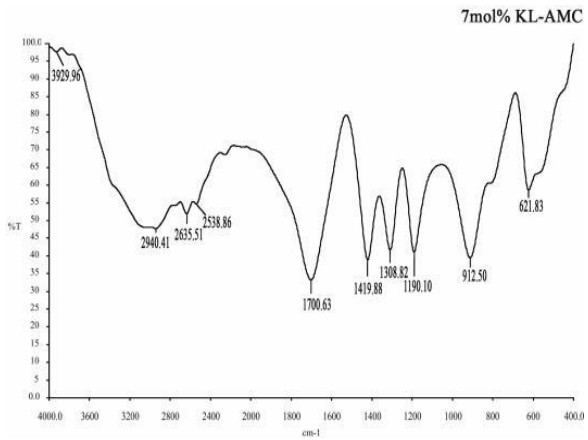
Table 3 Calculated optical energy gap for KL-AMC

System	Eg(ev)
KDP7mol% L-A	2.8
KDP13mol% L-A	3.0
KDP19mol% L-A	3.6
KDP23mol% L-A	3.1

3.3 FTIR Spectral Studies

L-Arginine is an amino acid having zwitter ionic character when it is dissolved in polar solvents. The addition of L-Arginine in KDP crystals expected to have remarkable effect due to polar interaction. The vibration spectra of KDP with varying proportions of L-Arginine were tabulated with characteristic group frequencies assignments. The symmetry is distorted very much and hence the frequency is shifted to lower region due to dipole – dipole interaction of zwitter ionic amino acid nature. Hence the stability of KDP is enhanced by the addition of L-Arginine as dopant. The OH bonding is shifted to lower region and also C=O stretching in the region is shifted to longer wave length only for KDP mixed with 7 mol% of L-Arginine but in all the other cases (13 mol%,19 mol% and 23 mol%) there is slight variation. This shows that carboxylic end is not involved in dative bonding. It is shown in the Table 4





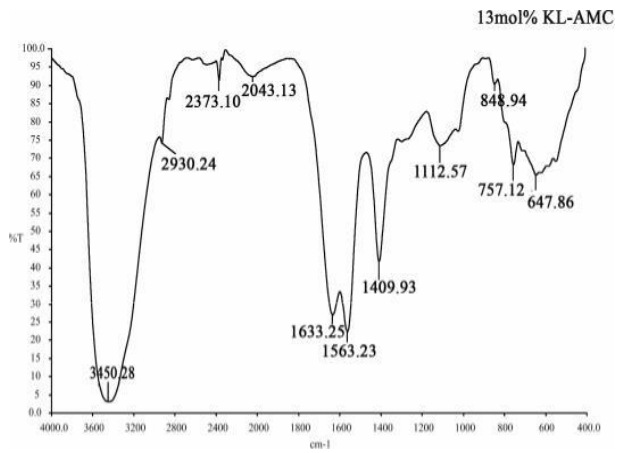


Fig 4.1 FT-IR Spectrum of L-Arginine, 7mol% and 13mol% KLAC

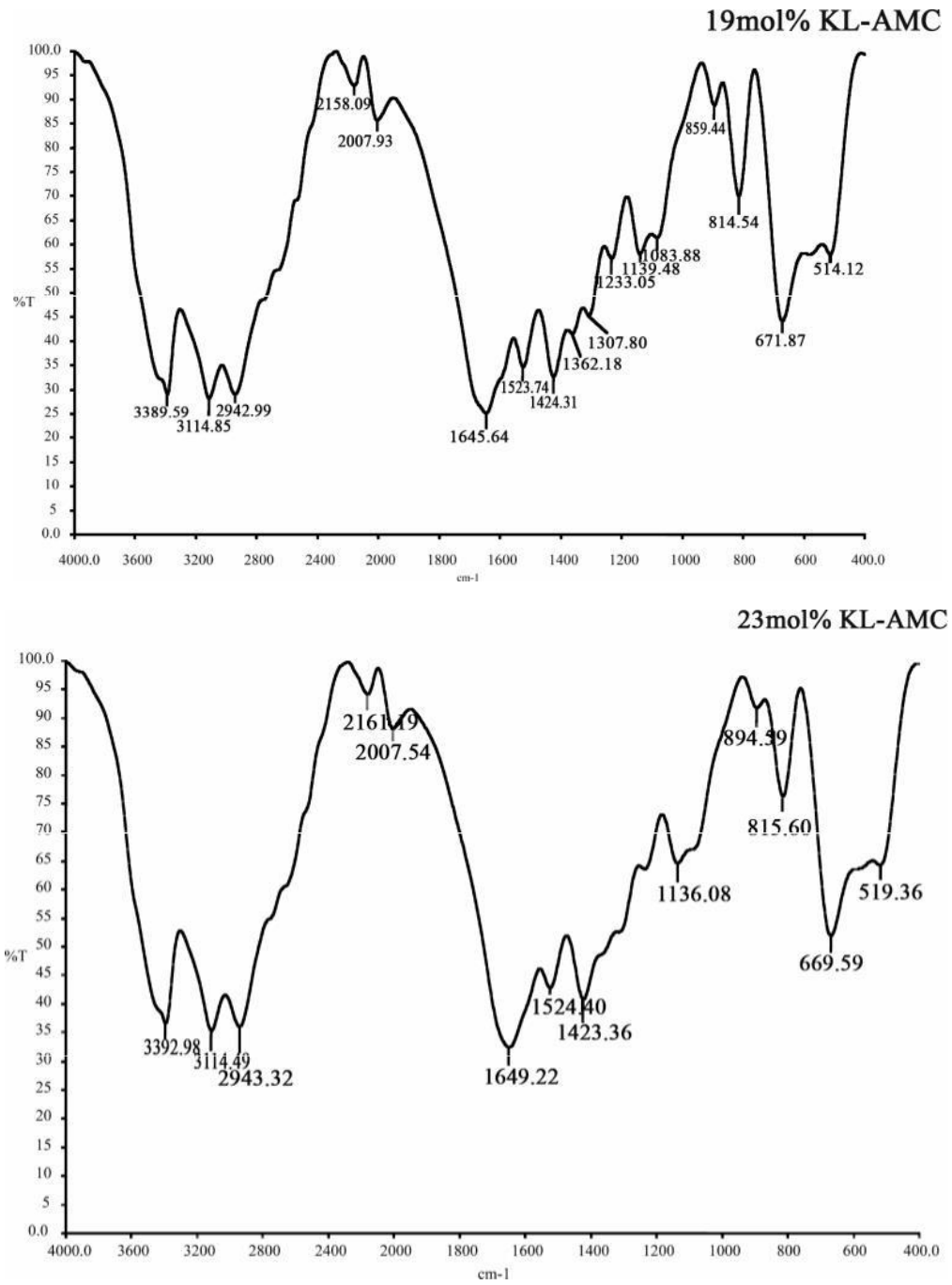


Fig 4.2 FT-IR Spectrum of 19mol% and 23mol% KLAC

Table : 4 Observed FT-IR frequency of KLAC (cm^{-1})

KDP	L-Ariginine	KDP 7 mol% L-Ariginine	KDP 13 mol% L-Ariginine	KDP 19 mol% L-Ariginine	KDP 23 mol% L-Ariginine	Assignment
3926	3969	3930	-	-	-	Free O-H stretching
3401	3057	-	3450	3390	3393	N-H stretching
2866	2634	2940	2930	2943	2843	P-H-O Asymmetric stretching
2455	2534	2636	2373	2158	2161	O ‖ P - OH stretching
1705	1700	1701	1635	1646	1649	C=O stretching
-	1418	1420	1409	1424	1423	COO-- asymmetric stretching

1298	1307	1309	-	1362	-	P=O stretching
1098	1197	1190	1113	1139	1136	C-N stretching
904	912	913	-	1084	909	N-H wagging & twisting
-	-	-	849	895	895	N-H wagging & twisting
-	798	-	757	-	-	N-H wagging & twisting
-	631	622	648	671	670	N-H wagging & twisting
545	-	-	-	574	519	N-H wagging & twisting

3.4. Single crystal x-ray diffraction

Lattice constant and cell volume of the mixed crystals are determined as KDP-L-Arginine by single crystal XRD analysis. The crystals data and structure refinement of mixed crystals are given in Table.5.

Table : 5 Unit cell parameters of KLAC

System	Determination from single crystal XRD				Inter axial angles	Crystal System
	a(Aº)	b(Aº)	c(Aº)	V(Aº)	(α, β and γ)	
KDP 7 mol% L-Ariginine	7.42	7.42	6.96	383	α = β = γ = 90˚	Tetragonal
KDP 13 mol% L-Ariginine	7.41	7.41	6.94	391	α = β = γ = 90˚	Tetragonal
KDP 19 mol% L-Ariginine	7.46	7.46	6.99	390	α = β = γ = 90˚	Tetragonal
KDP 23 mol% L-Ariginine	7.45	7.45	6.95	385	α = β = γ = 90˚	Tetragonal

3.5. Powder XRD analysis

Powder X-ray diffraction studies were carried out using rich seifert X-ray diffractometer employing CuKα (1.54058 Å) radiation. The powder pattern XRD specimen of KDP-L-Arginine mixed crystals have been indexed using checkcell software. The crystal system has not changed with the addition of L-Arginine in the KDP crystals, but the intensities of the peaks are 010, 020, 121, 231, 220, 112 and 251 and varied considerably. It is shown in Fig 5.1 – 5.4

Table 6.1 Calculated hkl values, 2θ and d spacing values for 7mol% KLAC

hkl Value	2θ cal	2θ exp	d cal	d exp
011	17.480	17.456	5.0693	5.0763
010	22.543	22.543	3.9875	3.9454
020	23.840	23.967	3.7293	3.7100
121	29.580	29.864	3.0174	2.9953
112	30.620	30.807	2.9173	2.9001
220	34.160	34.151	2.6226	2.6234
131	40.640	40.540	2.0465	2.1235
302	44.400	44.926	2.0386	2.0160
231	45.760	45.950	1.9812	1.9735
132	46.620	46.108	1.8455	1.9678

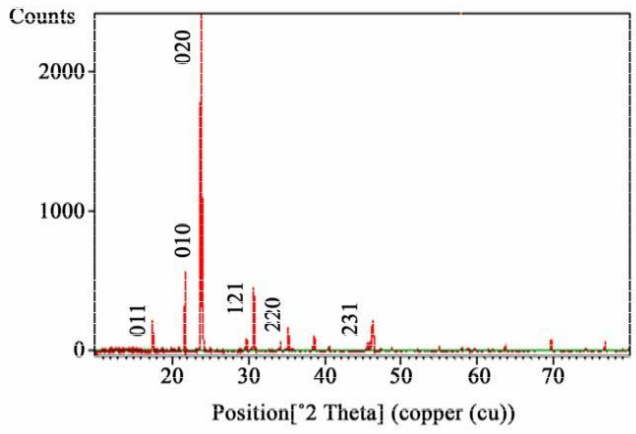


Fig 5.1 XRD Spectrum of 7mol% KLAC

Table 6.2 Calculated hkl values, 2θ and d spacing values for 13mol% KLAC

hkl Value	2θ cal	2θ exp	d cal	d exp
010	17.836	17.520	3.5543	3.5377
020	24.120	24.000	3.6867	3.7850
112	30.920	30.883	2.8896	2.8931
220	34.360	34.198	2.6078	2.6198
230	44.340	44.025	2.0413	2.0552
231	46.100	46.021	1.9673	1.9706
312	47.060	47.919	1.9294	1.8969
024	58.600	58.714	1.5740	1.5712
051	64.140	64.212	1.4507	1.4492
251	69.880	60.599	1.3450	1.3497
351	74.640	74.083	1.2705	1.2500
035	79.720	79.077	1.218	1.2100

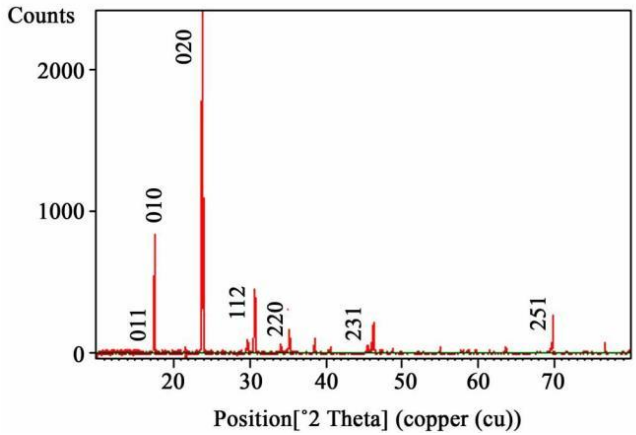


Fig 5.2 XRD Spectrum of 13 mol % KLAC

Table 6.3 Calculated hkl values, 2θ and d spacing values for 19mol% KLAC

hkl Value	2θ cal	2θ exp	d cal	d exp
011	17.560	17.372	5.0464	5.1007
010	21.786	21.745	5.7450	5.7690
020	23.888	23.836	3.7332	3.7300
121	29.720	28.647	3.0035	3.0109
112	30.780	38.661	2.9025	2.9135
130	38.700	38.116	2.6196	2.3591
231	45.694	1.9763	1.9839	1.9939
131	46.520	56.401	1.9506	1.9553

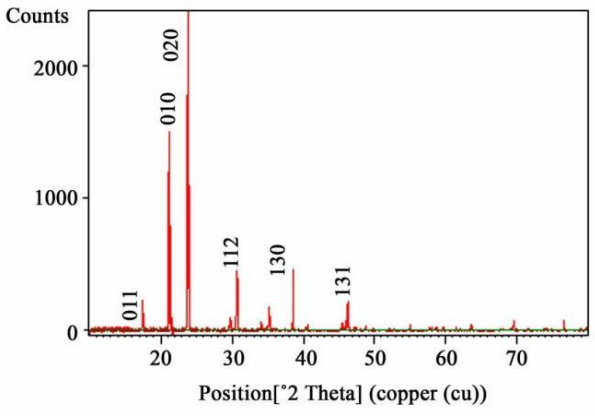


Fig 5.3 XRD Spectrum of 19 mol % KLAC

Table 6.4 Calculated hkl values, 2θ and d spacing values for 23mol% KLAC

hkl Value	2θ cal	2θ exp	d cal	d exp
011	17.520	17.339	5.0578	5.1103
010	21.534	21.536	3.9864	3.9780
020	23.094	23.580	3.7140	3.7880
112	30.680	30.686	2.8951	2.9112
132	46.640	46.133	1.9458	1.9660
133	55.400	55.240	1.6571	1.6615
151	64.160	64.301	1.4503	1.4463
251	68.680	68.279	1.3655	1.3726
115	69.860	69.877	1.3655	1.3450
044	74.600	74.162	1.2711	1.2776

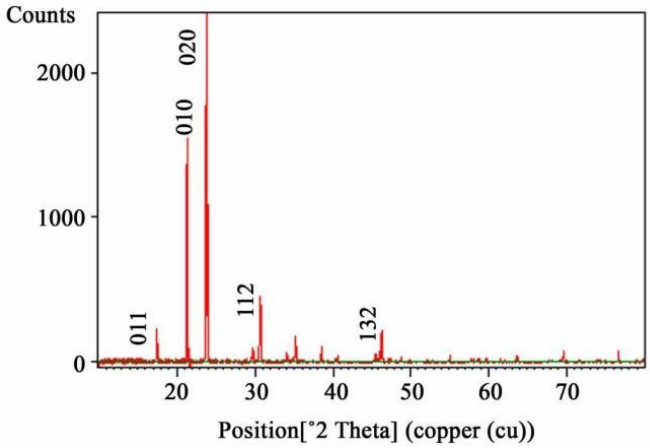


Fig 5.4 XRD Spectrum of 23 mol % KLAC

4. Conclusion

Pure KDP, 7mol%, 13mol%, 19mol% and 23mol% L-Arginine doped KDPcrystals were grown in slow evaporation technique.Entry of amino acid into the lattice of pure KDP crystals influences the size, perfection, transparency of the grown crystals.The grown crystals were characterized using powder X-ray diffraction and the cell parameters were calculated for both pure and L-Arginine doped crystals.Functional groups and the modes of vibration of pure and doped crystals were identified by FTIR spectroscopy. The UV- Visible spectroscopy shows the optical transparency enhancement in the L-Arginine doped crystals than the pure KDP crystal. Thus the L- Arginine doped crystal increases the optical transparency.It has been observed that addition of amino acid enhances transparency,thermal stability and NLO efficiency of KDP crystals.

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