

# Effect of Glycine As an Impurity on The Structural and Optical Properties of KDP-ADP Mixed Crystals

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**ABSTRACT:** Pure and glycine added mixed crystals of potassium dihydrogen phosphate (KDP) and ammonium dihydrogen phosphate (ADP) (a total of 15) have been grown by the slow (free) evaporation method at room temperature. The grown crystals were characterized chemically, structurally, thermally and optically by carrying out X-ray diffraction, Fourier transform infrared spectral, atomic absorption spectroscopic, UV-visible spectral and second harmonic generation efficiency (SHG) measurements. Results of the present study indicate that both mixing and impurity addition tune significantly the optical absorption and SHG efficiency without distorting significantly the lattice structure.

**KEYWORDS:** Crystal growth, KDP-ADP mixed crystals, Doped crystals, X-ray diffraction, Optical properties.

## I. INTRODUCTION

Single crystals of potassium dihydrogen phosphate (KDP),  $\text{KH}_2\text{PO}_4$ , and ammonium dihydrogen phosphate (ADP),  $\text{NH}_4\text{H}_2\text{PO}_4$ , have drawn special attention of researchers due to their interesting properties: wide wavelength range of optical transparency, electro-optic, dielectric and nonlinear optical properties, and the possibility of growing easily the large size crystals. Numerous applications have been discussed in the field of science and technology in the past for over 60 years. Both belong to the tetragonal crystal system at room temperature and are isomorphous to each other [1]. For many emerging technologies, it is necessary to form hybrid materials (by impurity addition on forming mixed crystals). Single phased mixed crystals and impurity added crystals without any lattice distortion have physical properties related to those of the pure crystals. However, the mixed composition/impurity concentration dependence varies from system to system and from property to property. Once the trend in mixed composition dependence and/or impurity concentration dependence is established, we have a means to have a tailor-made crystal with a desired value for a given physical property. In some properties, these dependences are highly nonlinear and the magnitude of the physical property may vary significantly from those for the pure (end member) ones. In this case, it is as if we have a new crystal in the family [2].

Several researchers have grown and characterized pure and impurity added KDP and ADP single crystals and reported several interesting results [3-16]. Growth and characterization of KDP-ADP mixed crystals have also been reported [17-20]. Aiming at discovering new materials, a research program was planned and a series of investigations have been carried out in our laboratories on the growth and properties of KDP and ADP single crystals. Mahadevan and his co-workers have already reported several useful results [1,21-26]. As a part of the program, glycine added (0.005 and 0.010 M are the concentrations considered) mixed crystals of KDP and ADP ( $\text{K}_{(1-x)}(\text{NH}_4)_x\text{H}_2\text{PO}_4$  with  $x = 0.0, 0.25, 0.50, 0.75$  and  $1.0$ ) have been grown by the slow (free) evaporation method at room temperature and characterized chemically, structurally, and optically. Herein the results obtained in the present study are reported and discussed.

**II. MATERIALS AND METHODS****2.1 Crystal growth**

Analytical reagent (AR) grade samples of KDP, ADP and glycine along with double distilled water were used in the present study for the growth of single crystals.

Aqueous solution of  $K_{(1-x)}(NH_4)_xH_2PO_4$  doped with glycine was prepared at a supersaturated concentration and taken in the nucleation cell (corning glass vessel of volume 100ml) and allowed to equilibrate at the desired temperature. The crystals were grown in the unstirred condition by the slow (free) evaporation method. Small crystals appeared in the beginning due to slow evaporation of solvent and grew larger in about two weeks time. Best crystals were selected from this and used for the characterization experiments. The temperature and volume were kept constant respectively at 30 °C and 25 ml in all the crystal growth experiments.

Crystals were grown from three mixed solutions (with x values 0.75, 0.50 and 0.25) along with two end member solutions (i.e. with x values 0.0 and 1.0). Glycine was added in two different molar concentrations, viz. 0.005 and 0.010 M. A total of 15 crystals (5 undoped + 10 doped) were grown in the present study. Concentration programming was done to get good quality crystals by using various supersaturated concentrations between 2.2 and 3.8 M. The optimized concentrations considered are 2.5, 2.75, 3.0, 3.25 and 3.5 M respectively for the supersaturated aqueous solutions having x values 0.0, 0.25, 0.5, 0.75 and 1.0.

**2.2 Characterization**

Densities of the grown crystals were measured by the floatation method [2] within an accuracy of  $\pm 0.008 \text{ g/cm}^3$ . Carbon tetrachloride of density  $1.594 \text{ g/cm}^3$  and bromoform of density  $2.890 \text{ g/cm}^3$  are respectively the rarer and denser liquids used. Atomic absorption spectroscopic (AAS) measurements were carried out for all the mixed (undoped) crystals using an atomic absorption analyzer (Model AA-6300) to determine the K atom content in the mixed crystals. The natural impurities present in the crystal (Fe, Mg and Na) were also determined by AAS analysis.

X-ray diffraction (XRD) data were collected at room temperature (25 °C) from powder diffractometer (X-PERT PRO PANalytical) with monochromated  $CuK\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) in the  $2\theta$  range 10-80°. The observed reflections were indexed following the procedures of Lipson and Steeple [27]. Lattice parameters were determined for all the fifteen crystals grown from the indexed data using high angle reflections by considering a set of two reflections and forming two simultaneous equations using the relation,

$$(4 \sin^2\theta) / \lambda^2 = (h^2 + k^2) / a^2 + l^2 / c^2 \quad \dots\dots\dots (1)$$

( $\lambda$  is the wavelength of radiation, h, k and l are the indices of reflection and a and c are the lattice parameters) and solving the same for the unknown lattice parameters. Several sets were considered in each case and the averages of 'a' and 'c' values obtained are reported.

Fourier transform infrared (FTIR) spectra were recorded in the wavenumber range 400 – 4000  $\text{cm}^{-1}$  by the KBr pellet method for all the fifteen crystals grown using a Perkin Elmer FTIR spectrometer.

UV-visible absorbance spectra for all the fifteen crystals grown (dissolved in water) were recorded in the wavelength range 200 – 800 nm using a Varian Cary Eclipse spectrometer. The second harmonic generation (SHG) efficiency was determined for all the fifteen crystals grown (powder samples used) by the Kurtz and Perry method [28] using a Q-switched Nd:YAG laser ( $\lambda = 1064 \text{ nm}$ ) (supplied by Spectra Physics, USA). The SHG output from the powder sample was compared with that from KDP and the results were obtained in terms of KDP unit.

**III. RESULTS AND DISCUSSION****3.1 Densities, lattice parameters and chemical composition**

The single crystals grown in the present study can be represented as

- KA (1)  $K_{(1-x)}(NH_4)_xH_2PO_4$  with x = 0.0
- KA (2)  $K_{(1-x)}(NH_4)_xH_2PO_4$  with x = 0.25
- KA (3)  $K_{(1-x)}(NH_4)_xH_2PO_4$  with x = 0.50
- KA (4)  $K_{(1-x)}(NH_4)_xH_2PO_4$  with x = 0.75
- KA (5)  $K_{(1-x)}(NH_4)_xH_2PO_4$  with x = 1.0
- KA (6) KA (1) added with 0.005 M glycine
- KA (7) KA (2) added with 0.005 M glycine

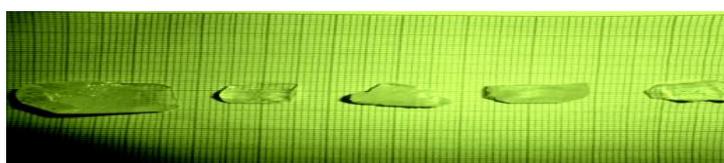
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KA (8)	KA (3)	added with 0.005 M glycine
KA (9)	KA (4)	added with 0.005 M glycine
KA (10)	KA (5)	added with 0.005 M glycine
KA (11)	KA (1)	added with 0.010 M glycine
KA (12)	KA (2)	added with 0.010 M glycine
KA (13)	KA (3)	added with 0.010 M glycine
KA (14)	KA(4)	added with 0.010 M glycine
KA (15)	KA (5)	added with 0.010 M glycine

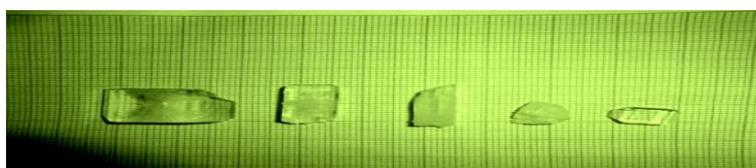
Photographs of the sample crystals grown in the present study are shown in Figure 1. All the fifteen crystals grown are stable under atmospheric conditions, colourless and transparent. Mixing leads to morphological changes.



(a) From left to right : KA(1), KA(2), KA(3), KA(4), KA(5)



(b) From left to right : KA(6), KA(7), KA(8), KA(9), KA(10)



(c) From left to right : KA(11), KA(12), KA(13), KA(14), KA(15)

**Figure 1: Photographs of the sample crystals grown**

The densities and K atom contents observed in the present study are given in Table 1. The chemical (mixed) compositions estimated using the measured densities and using the K atom contents obtained through AAS measurements are also given in Table 1. The density values obtained in the present study for KDP and ADP compare well with those reported in the literature [29,30]. Densities of the mixed crystals have been found to be very nearly additive obeying the relation,

$$d = xd_1 + (1-x)d_2 \quad \dots\dots\dots (2)$$

where d is the density of the mixed crystal and d<sub>1</sub> and d<sub>2</sub> are respectively the densities of ADP and KDP.

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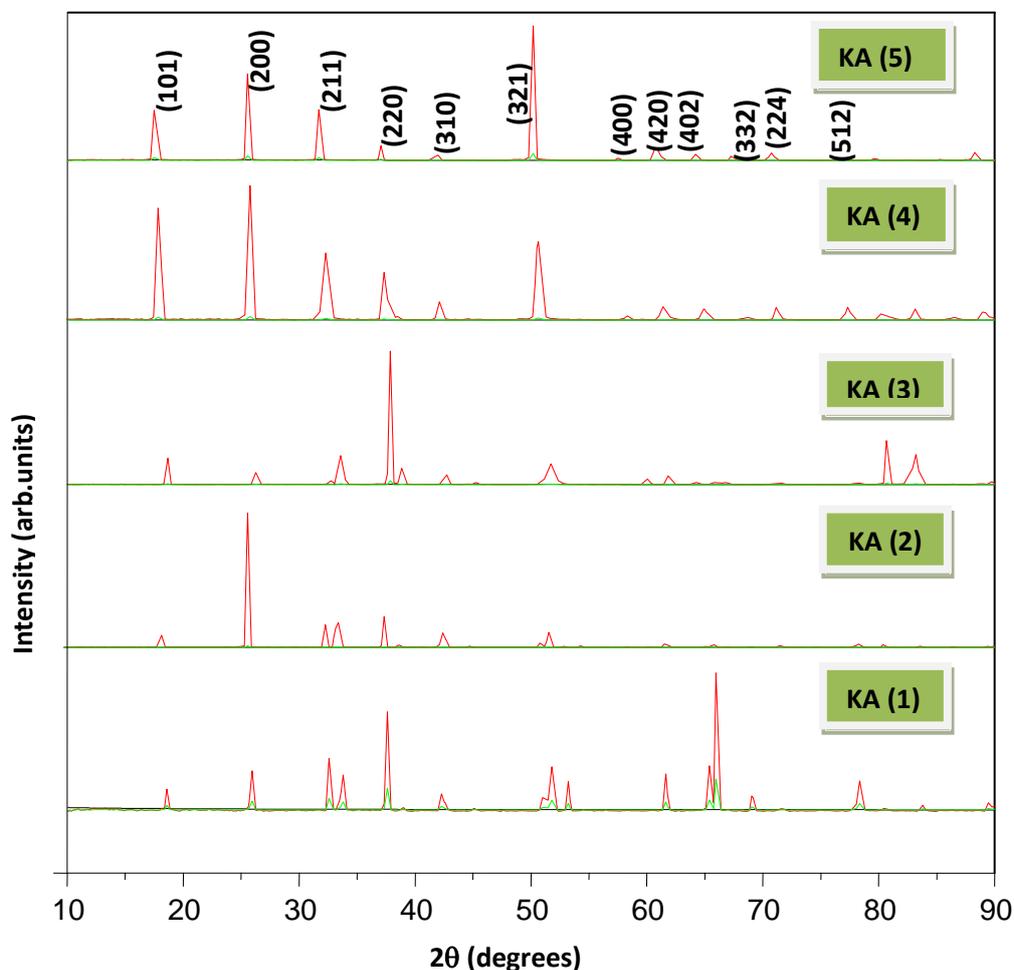
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**Table 1**

The densities, metal atom contents and chemical compositions observed for the undoped mixed KDP-ADP crystals grown in the present study

Crystal	Density (g/cm <sup>3</sup> )	K content (%)	Mg (ppm)	Na (ppm)	Fe (ppm)	Chemical Composition (x) from	
						Density data	AAS ata
KA (1)	2.922	-	50	100	20	-	-
KA (2)	2.253	98.7	9	16	6	0.54	0.51
KA (3)	2.157	90.6	12	34	3	0.66	0.91
KA (4)	2.093	50.9	8	22	2	0.84	0.99
KA (5)	1.903	-	-	50	10	-	-

The mixed composition (x) obtained in the present study using the density values compare nearly with that obtained using K atom contents determined through AAS measurements.



a) For undoped KDP-ADP mixed crystals

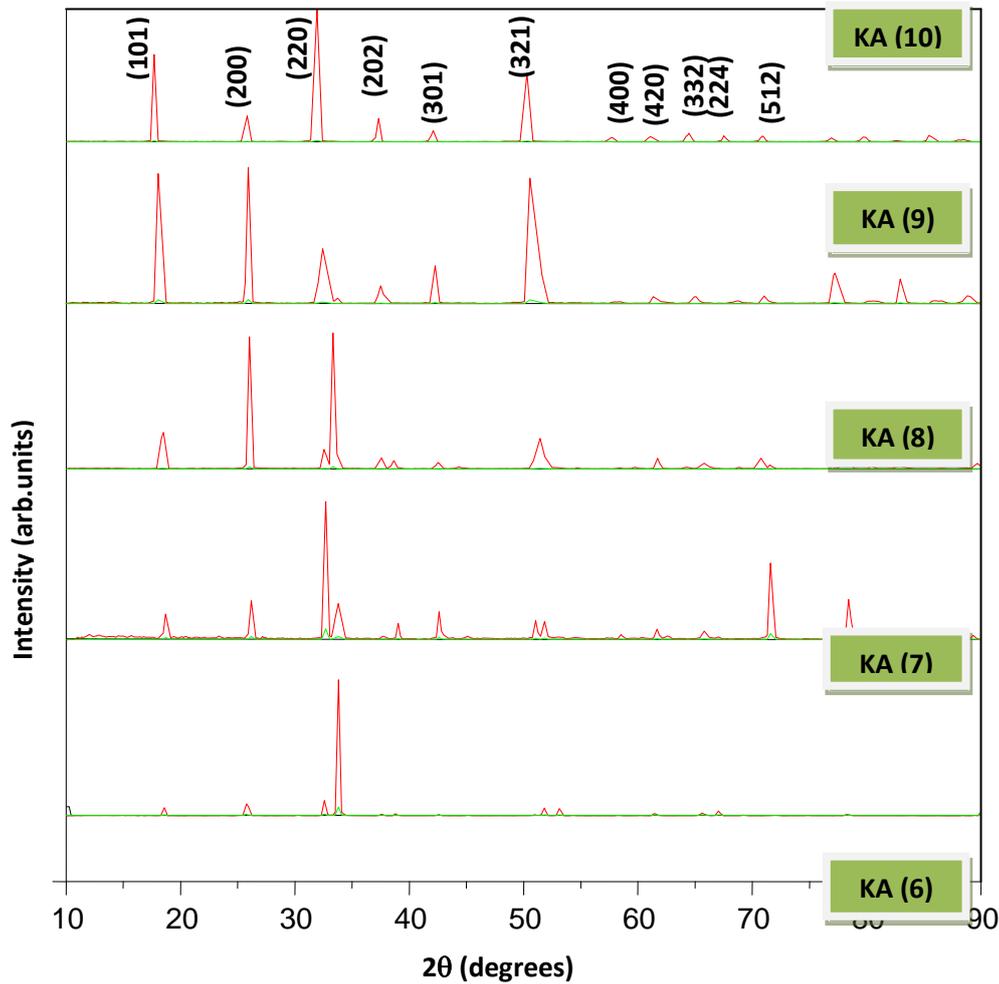
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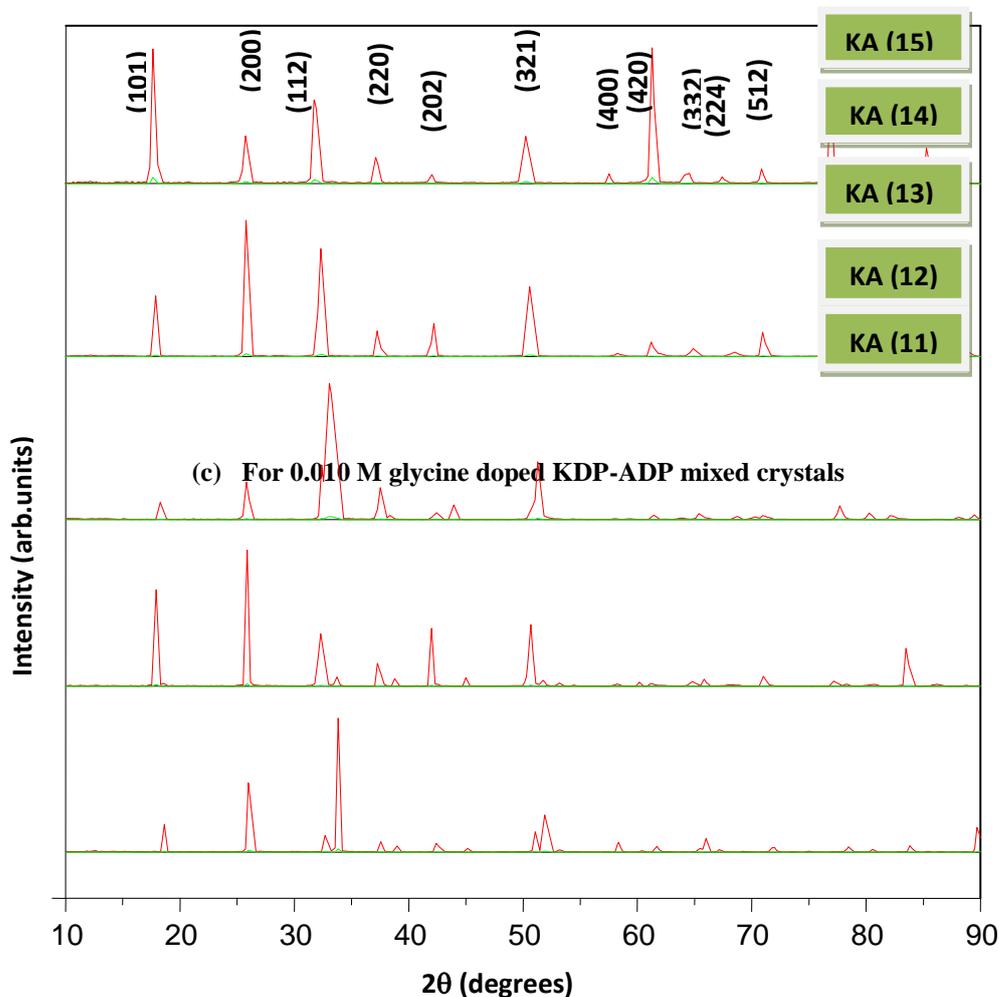
As glycine is an organic substance, no experiment was carried out to determine the impurity content in the doped crystals.

The XRD patterns recorded in the present study for all the fifteen crystals grown are shown in Figure 2. Appearance of strong and sharp peaks confirms the crystalline nature of the samples.



(b) For 0.005 M glycine doped KDP-ADP mixed crystals

The XRD peaks were indexed for the tetragonal system and the lattice parameters obtained through XRD analysis are given in Table 2. The lattice parameters obtained for KDP and ADP are in good agreement with those reported in the literature [31, 32].



**Figure 2 : The observed XRD patterns**

Replacement of  $K^+$  by  $(NH_4)^+$  and glycine doping have not distorted the crystal structure significantly. So we can understand that the mixed crystals grown in the present study are single phased. Small changes in  $2\theta$  and peak intensity observed due to doping with glycine indicate that the glycine molecules have entered into the host crystal matrix.

**Table 2**

The lattice parameters estimated for all the fifteen mixed KDP-ADP crystals grown in the present study

Sample	a = b (Å)	c (Å)	Volume (Å <sup>3</sup> )
KA (1)	7.433	6.963	384.7
KA (2)	7.454	6.991	388.4
KA (3)	7.382	6.884	375.1
KA (4)	7.463	7.186	400.2

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KA (5)	7.518	7.628	431.1
KA (6)	7.438	6.856	379.3
KA (7)	7.346	6.882	371.4
KA (8)	7.399	6.918	378.7
KA (9)	7.422	7.249	399.3
KA (10)	7.475	6.214	347.2
KA (11)	7.410	6.952	381.7
KA (12)	7.427	7.295	402.4
KA (13)	7.424	7.089	390.7
KA (14)	7.455	7.133	396.4
KA (15)	7.468	7.748	432.1

**Table: 3**

Band assignments for undoped KDP-ADP mixed crystals

Sl. No.	KA(1)	KA(2)	KA(3)	KA(4)	KA(5)	Assignment
1.	3665	3664	3668	3641	3668	O-H stretching
2.	-	3252	3253	3266	3267	O-H stretching
3.	-	2482	2480	2480	2482	O=P-OH asymmetric stretching
4.	2360	2375	-	2350	2350	P-O-H bending
5.	-	1726	1730	1729	1728	N-H stretching
6.	1635	1645	1647	1640	1636	O=P-OH asymmetric stretching
7.	-	1450	1451	1458	-	N-H stretching
8.	1299	1298	1294	1290	1296	P=O stretching
9.	1101	1092	1092	1100	1085	SP=O stretching
10.	902	900	902	904	906	P=O stretching
11.	534	533	538	558	556	HO-P-OH bending

The band assignments are provided in Tables 3-5. As in the case of XRD patterns, the FTIR spectra observed indicate that the mixed crystals grown contain both the potassium and ammonium components.

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**Table: 4**  
Band assignments for 0.005 M glycine doped KDP-ADP mixed crystals

Sl. No	KA(6)	KA(7)	KA(8)	KA(9)	KA(10)	Assignment
1.	-	-	3250	3248	3242	O-H stretching
2.	2458	2456	2456	2445	2455	O=P-OH asymmetric stretching
3.	2332	2328	2386	2388	2386	P-O-H bending
4.	-	-	1452	1446	1446	N-H stretching
5.	-	1310	1310	1312	1315	C-H bending
6.	1100	-	1110	1115	1113	C-C stretching
7.	-	1096	-	-	-	P=O stretching
8.	901	-	916	898	883	P-O-H stretching
9.	530	527	536	544	549	HO-P-OH bending
10.	455	456	459	456	456	O-P-O bending
11.	-	407	403	-	-	N-H torsional oscillations

Also, the FTIR spectra recorded for the doped crystals indicate the presence of glycine molecules in the crystal matrix. This is evidenced by the presence of absorption in the wavenumber regions 1100-1115 (C-C stretching) and 1310-1315(C-H bending) in the case of doped crystals.

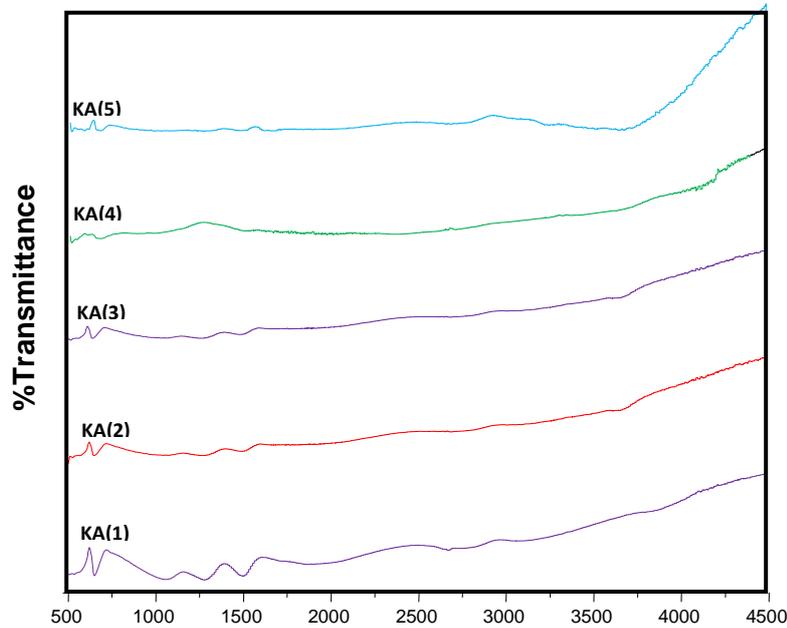
**Table: 5**  
Band assignments for 0.010 M glycine doped KDP-ADP mixed crystals

Sl. No.	KA(11)	KA(12)	KA(13)	KA(14)	KA(15)	Assignment
1.	3745	3753	3749	3754	3750	O-H stretching
2.	3655	3656	3660	3653	3656	O-H stretching
3.	2332	2328	2386	2388	2386	P-OH bending
4.	-	-	1452	1446	1446	N-H stretching
5.	-	1310	1310	1312	1315	C-H bending
6.	1100	-	1110	1115	1113	C-C stretching
7.	-	1096	-	-	-	P=O stretching
8.	901	-	916	898	883	P-O- H stretching
9.	530	527	536	544	549	HO-P-OH bending
10.	455	456	459	456	456	O-P-O bending
11.	-	407	403	-	-	N-H Torsional oscillations

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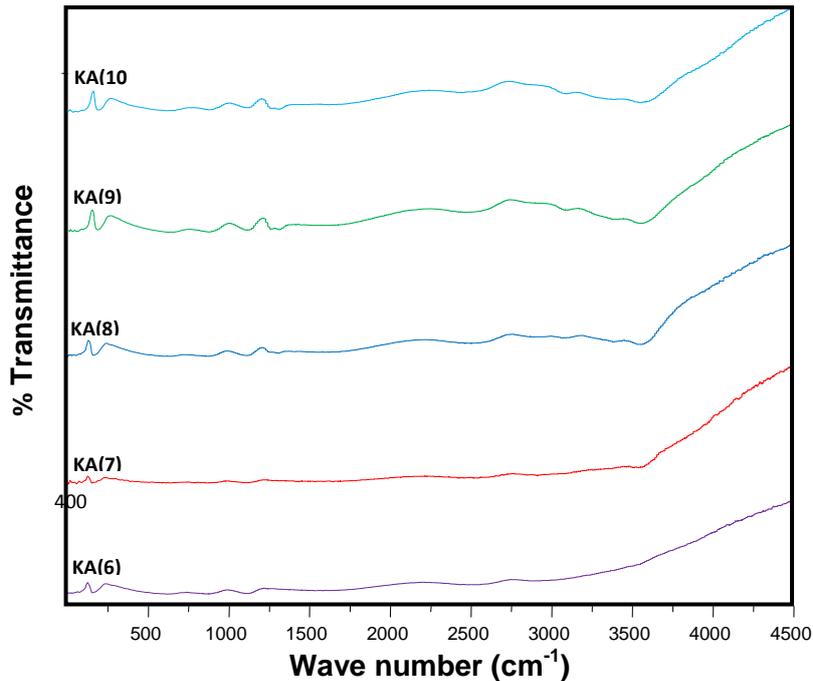
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(a) For undoped KDP-ADP mixed crystals

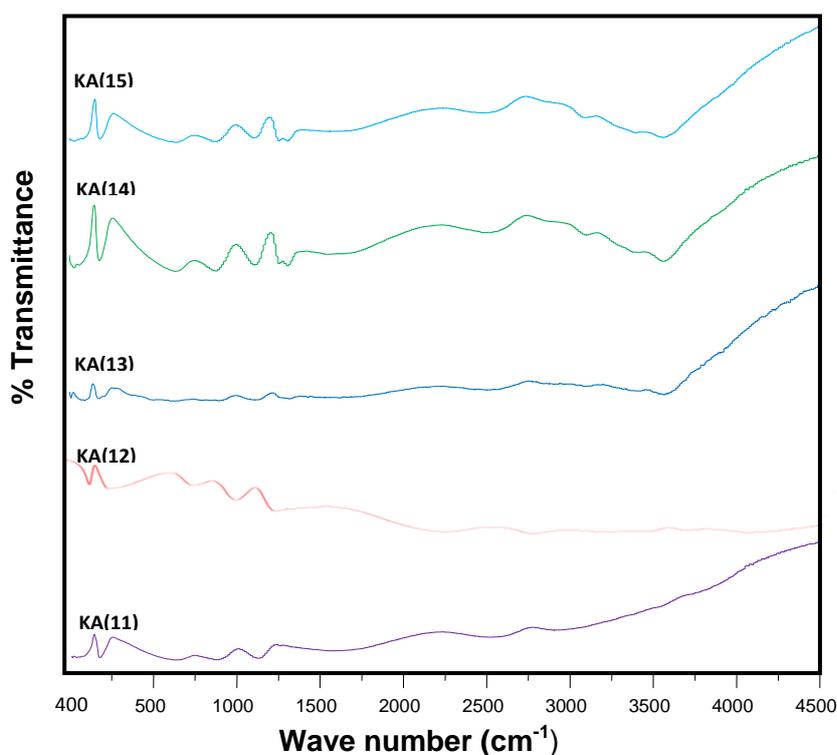
Wave number (cm<sup>-1</sup>)

The FTIR spectra recorded for all the fifteen crystals grown are shown in Figure 3. The band assignments were made on the basis of relative intensities, magnitudes of wavenumbers and literature data [31,32].



(b) For 0.005 M glycine doped KDP-ADP mixed crystals

In effect, the present study indicates that the ammonium ion is able to replace the potassium ion in a better way so that, in the mixed crystals, the  $\text{NH}_4^+$  component(x) is more than that considered in the aqueous solution used for the growth of mixed crystals.



(c) For 0.010 M glycine doped KDP-ADP mixed crystals

**Figure 3: The observed FTIR patterns**

Moreover, the AAS data indicate the presence (at ppm level) of natural impurities like Mg, Na and Fe atoms which were present in small quantities in the KDP and ADP salts used for the growth of single crystals. In addition, mixing leads to reduction of natural impurities present.

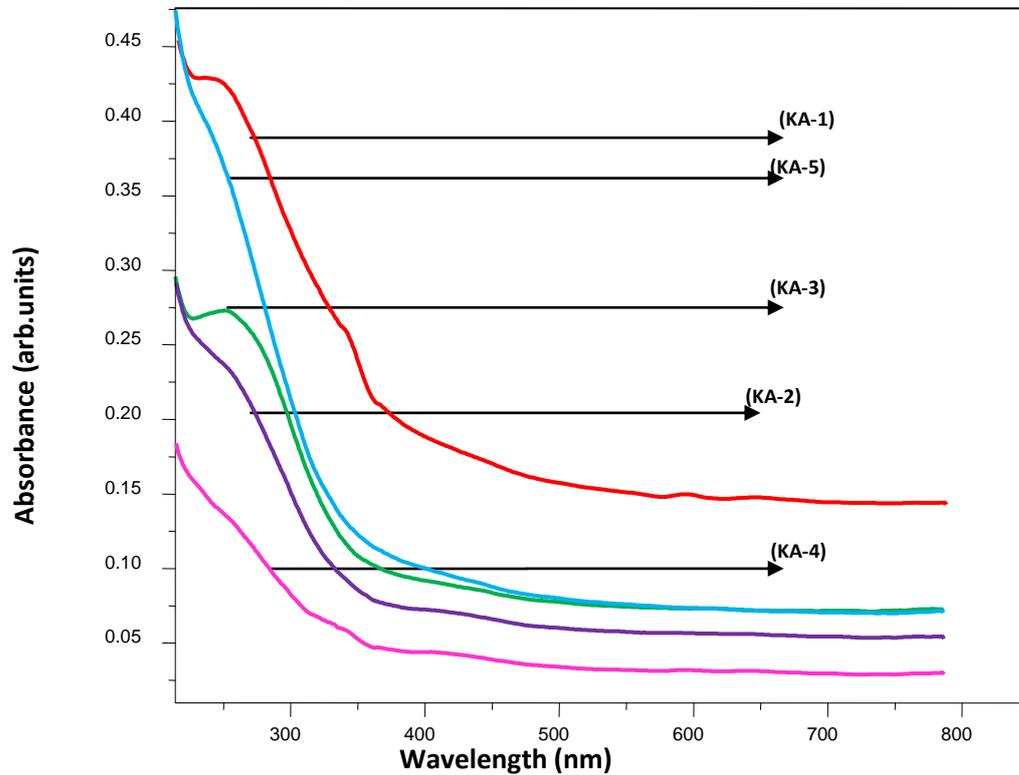
### 3.2 Optical properties

For NLO materials, the optical transmission (wavelength) range and the transparency cut off limits (absorption edges) are considered to be important. These materials can be put into use only if they possess the required cut-off wavelength as well as low absorption. The UV-visible spectra recorded in the present study are shown in Figure 4.

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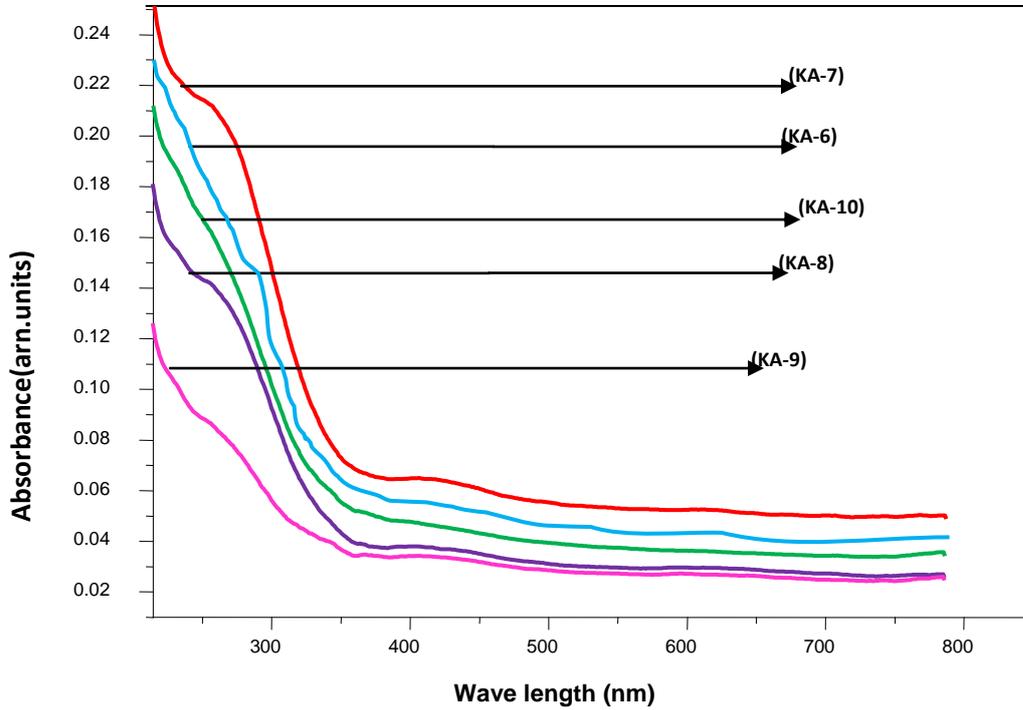
(a) For undoped KDP-ADP mixed crystals

The observed spectra indicate that all the 15 crystals grown in the present study exhibit good transparency in the entire visible region. The transmittance is minimum for KA1(pure KDP) and KA5(pure ADP) crystals. Mixing is found to improve the transmittance but nonlinearly with the composition. KA4 exhibits maximum transmittance.

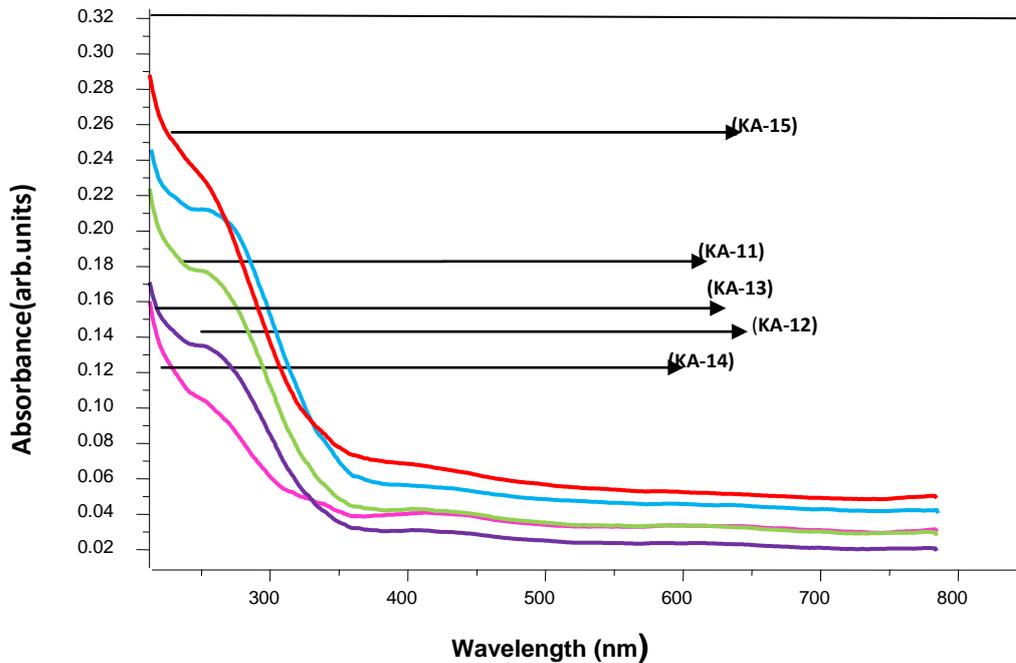
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(b) For 0.005 M glycine doped KDP-ADP mixed crystals



(c) For 0.010 M glycine doped KDP-ADP mixed crystals

Figure 4 : The observed UV-visible patterns

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Further, doping with glycine significantly improves the transmittance. The absorption edges lie nearly within the wavelength range 300-350nm. The good transparency observed in the visible region for all the crystals grown is a desirable property for NLO applications.

**Table: 6:** SHG efficiencies of all the grown crystals (in KDP unit)

Crystal	SHG efficiency	Crystal	SHG efficiency	Crystal	SHG efficiency
KA(1)	1.00	KA(6)	0.88	KA(11)	0.84
KA(2)	0.89	KA(7)	0.86	KA(12)	0.78
KA(3)	0.86	KA(8)	0.83	KA(13)	0.75
KA(4)	0.84	KA(9)	0.81	KA(14)	0.74
KA(5)	0.81	KA(10)	0.80	KA(15)	0.70

The SHG efficiencies observed in the present study are given in Table 6. It can be observed that the SHG efficiency increases with the increase in KDP content but decreases with the increase in glycine concentration. It is interesting to note that all the 15 crystals grown in the present study are NLO active. Further, the present study indicates that the optical properties (optical transmittance and SHG efficiency) are tuned significantly by mixing KDP and ADP as well as by doping with glycine.

### IV. CONCLUSIONS

Pure and glycine added  $(KDP)_{(1-x)}(ADP)_x$  single crystals (a total of 15) have been successfully grown at room temperature by the free evaporation method. The XRD, density, AAS and FTIR spectral measurements indicate the formation of mixed and doped crystals as expected without any lattice distortion. The optical measurements indicate that mixing KDP with ADP and doping with glycine lead to significant changes of optical transmittance and SHG efficiency.

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