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Effect of trytophan as dopant on potassium acid phthalate single crystals

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Optically transparent single crystals of potassium acid phthalate (KAP, 0.5 g) 0.05 g and 0.1 g (1 and 2 mol %) trytophan were grown in aqueous solution by slow evaporation technique at room temperature. Single crystal X- ray diffraction analysis confirmed the changes in the lattice parameters of the doped crystals. The presence of functional groups in the crystal lattice has been determined qualitatively by FTIR analysis. Optical absorption studies revealed that the doped crystals possess very low absorption in the entire visible region. The dielectric constant has been studied as a function of frequency for the doped crystals. The thermal stability was evaluated by TG-DSC analysis.

Capsule Summary: Potassium acid phthalate in the presence of tryptophan were grown, using evaporation technique, characterized using advance techniques, results revealed the formation of single crystals in orthorhombic system and the amino acid in the KAP crystal lattice was incorporation successfully.

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INTRODUCTION

Amino acids like glycine (Sekar and Parimaladevi, 2009) and arginine (Murugakoothan et al., 1999) have higher SHG efficiency. The addition of amino acids in the semi inorganic material like KAP may perform modification or changes in the lattices or crystal behavior. Previously, un-doped and amino acid doped good quality single crystal of sodium acid phthalate crystal has been reported by Nirmala et al. (2013). Authors also used slow evaporation for the growth of crystals. The effect of amino acid as dopant on the growth and the properties of sodium acid phthalate single crystal was investigated. The results of FT-IR study confirmed the presence of amino acids in the doped crystals, TGA/DTA revealed that the crystal were thermally stable due to the doping of L-valine and amino acid additives did not destroy the optical transparency of the crystals. The mechanical property of the doped crystal was also increased due to the doping of L-valine. Other researcher also performed similar studies such as growth and characterization of potassium acid phthalte (Sivakumar et al., 2012) and compared pure and deuterated potassium acid phthalate single crystals on the basis of advanced characterization techniques (Kumar et al., 2002) and the use of tryptophan for the growth of potassium acid phthalate single crystal has not been studied in detail. Hence, the effect of amino acids such as tryptophan as additives on the growth, morphology, structural, optical,

Fig. 1: Photograph of 1 mol % KAPT

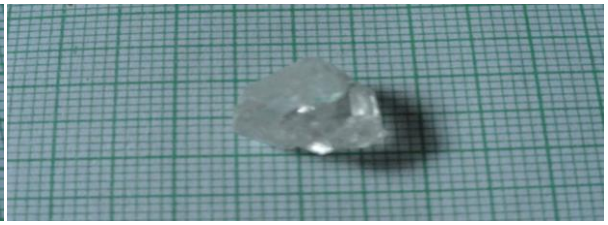

Fig. 2: Photograph of 2 mol % KAPT

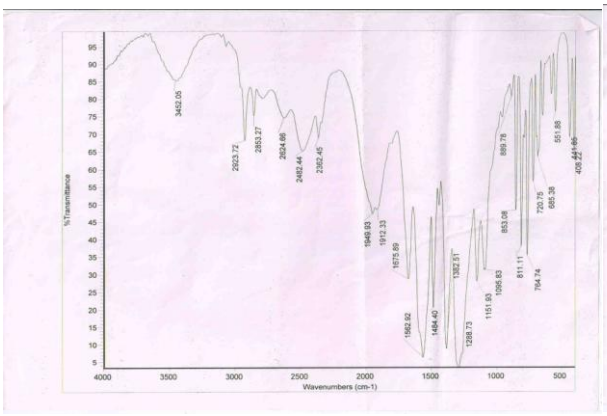

Fig. 3: FTIR Spectrum of 1 mol % KAPT

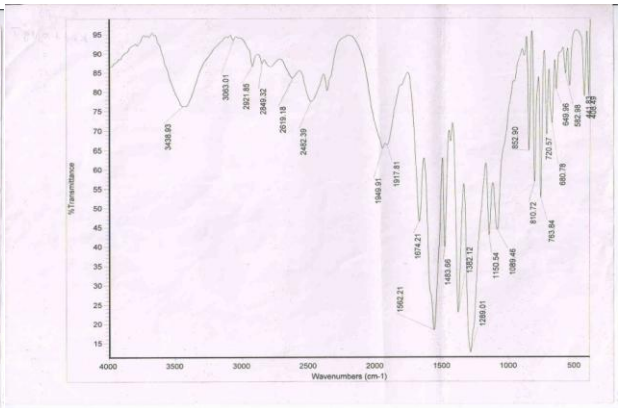

Fig. 4: FTIR Spectrum of 2 mol % KAPT

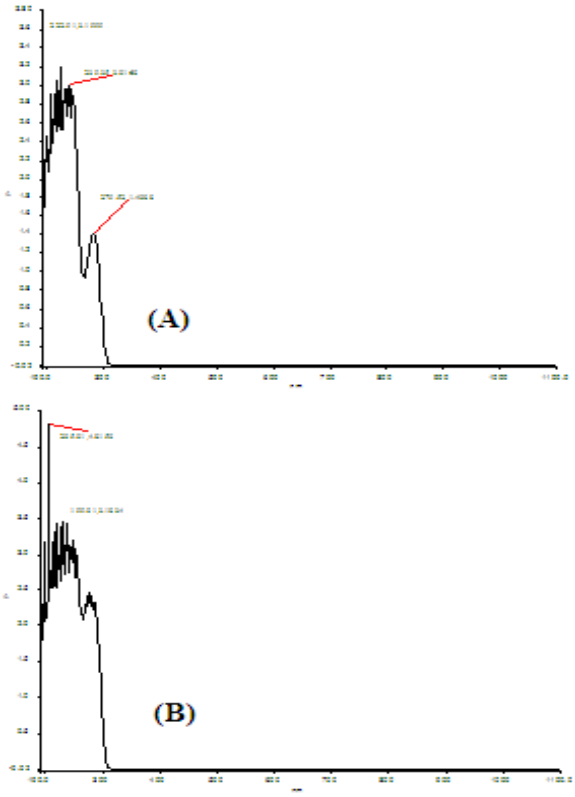

Fig. 5: UV spectrum of CAP doped tryptophan

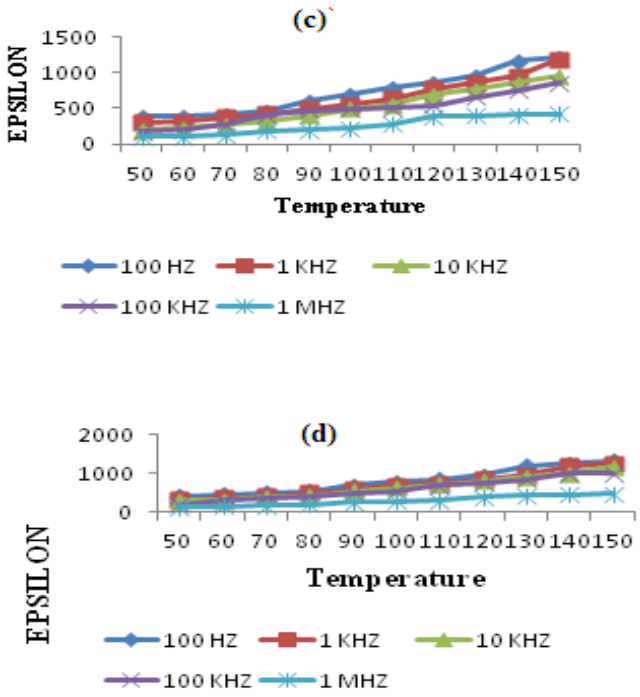

Fig. 6: Temperature Vs dielectric constant: (c) 1 mol % (d) 1 mol % KAPT

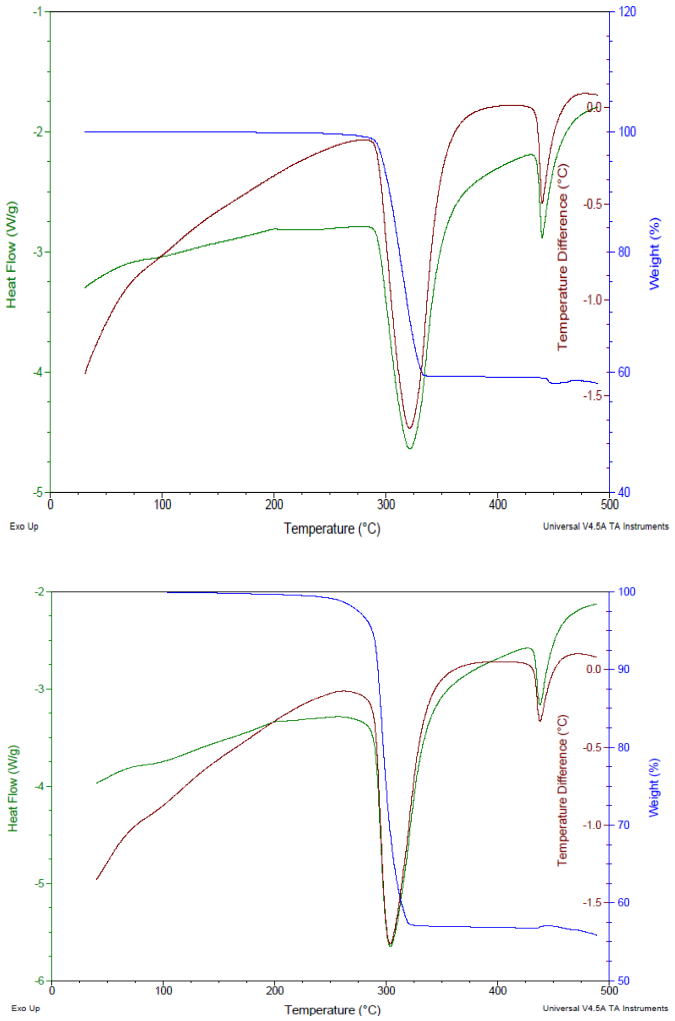

Fig. 7: TGA – DSC of 1and 2 mol % KAPT

thermal and mechanical properties of KAP crystals was investigated in present study.

EXPERIMENTAL

A saturated solution of KAP was prepared in 2 beakers. Tryptophan was taken dopant with 1 mol % and 2 mol % by weight in the mother solution. The solution was filtered with a microfilter. The seed crystals are allowed to float on the surface of the saturated solution and left for slow evaporation at room temperature. The crystallization took place within three weeks and the optically transparent crystals of Tryptophan doped KAP (KAPT) were obtained and harvested. The harvested crystals of 1 mol % KAPT and 2 mol % KAPT were shown in fig 1,2 respectively .The size of the crystals were 3 cm and 2 cm, respectively.

RESULTS AND DISCUSSION

X-ray diffraction studies

The single crystal X- ray diffraction analysis of KAPT was recorded using ENRAF NONIUS CAD-4 X-ray diffractometer. This analysis has revealed that the single crystals of doped KAP crystallize in orthorhombic system. The calculated lattice parameters for different proportions of KAPT are given in Table 1. The XRD analysis have confirmed the incorporation of amino acid in KAP crystal lattice.

FTIR spectral analysis

The FTIR spectra for KAPT at 1 mol %, 2 mol % were recorded using Bruker IFS 66 V spectrometer in the range 4000 – 400 cm^{-1} employing KBr pellet technique and results are shown in Figs. 3 and 4, respectively. The IR absorption frequencies are shown in Table 2.

UV analysis

The UV spectrum of KAP doped Tryptophan at 1 mol % and 2 mol % were carried out using a double beam spectrophotometer in the range of 200nm – 1100nm and shown in Figs. 5ab.The absorption at λ_{max} 222 nm for 1 mol % KAPT, 205.01 nm for 2 mol % KAPT shows the five membered heteroatom in tryptophan is linked with six membered aromatic ring. For 1 mol % KAPT, observed λ_{max} values are 222.91 nm and 239.35 nm are due to π - π^* transitions, n-π^* transitions occurs at 279.5 nm. For 2 mol % of KAPT due to σ - σ^* transition the λ_{max} values occurs at 199.01 nm. The observed λ_{max} values are shown in Table 3 (1 and 2 mole % KAPT).

Conductivity studies

The dielectric constant of materials is due to electronic, ionic, dipolar and space charge polarizations, which depend on the frequencies (Dharmaprakash and Rao, 1989). At low frequencies, all these polarizations are active. The dielectric constants were calculated for 1 mol % KAPT, 2 mol % KAPT and results are depicted in the Table 4 and 5, respectively. Graphs were drawn connecting ε_r Vs temperature and are was shown in Figs. 6ed.

DSC and TGA analysis

The TG – DSC analysis were carried out by using a NETZSCH STA 409 °C thermal analyser in nitrogen atmosphere of KAPT at two different proportions are shown in Fig. 7. In 1 mol % KAPT, one molecule of water is lost on heating at 289 °C to 323 °C. This accounts for the 36% mass loss observed in the TGA curve. For 2 mol %, the mass loss was 43% and the decomposition temperature at 251 °C. In different proportions of KAPT, there is weight loss at 326 °C

Table 1: Crystallographic parameters of KAPT

S # No	Parameters	1 mol % KAPT	2 mol % KAPT
1.	a	6.38	6.45
2.	b	9.38	9.54
3.	c	13.19	13.25
4.	Volume	789 A°	817 A°

Table 2: Infrared Absorption Frequencies of KAPT Crystal

Wavenumber cm^{-1}		
1 mol % KAPT	**2 mol % KAPT**	**Assignments**
3452	3438	OH stretching
2923	2921	CH symmetric stretching
2624	2619	Intramolecular H-bonding with C=O
2482.44	2482.39	Asymmetric strong NH_2 stretching
1949.93	1949.21	= C-H out of plane bending
1675.89	1675.21	N-H stretching vibration
1484.40	1483.66	C=C ring stretching
1288.73	1289.01	-C=O carboxylate ion =O asymmetric stretching
1095.83	1089.46	Asymmetric C-O-C stretching
811.11	810.72	C-H out of plane bending

Table 3: Observed λ_{max} values of KAPT

1 mol % KAPT	2 mol % KAPT	Assignment
-	199.01	σ - σ^*
222.91		
	205.01	π - π^*
& 239.35		
279.52	-	n - π^*

Table 4: Dielectric Constant Values of 1 mol % KAPT

	ε_r for various frequencies				
Temp ℃	100HZ	1KHZ	10KHZ	100KHZ	1MHZ
150	1219.37	1192.54	956.64	856.64	418.29
140	1172.72	955.54	859.74	756.56	409.54
130	958.72	864.72	764.64	654.32	394.32
120	864.64	772.64	698.54	539.13	381.55
110	794.65	634.64	555.19	500.59	274.72
100	695.64	555.55	498.72	490.15	215.15
90	598.18	498.65	398.16	465.26	194.49
80	458.64	419.15	310.99	410.55	185.65
70	409.84	372.49	272.54	265.85	119.72
60	392.15	316.15	219.34	200.19	100.49
50	383.14	298.43	198.15	172.15	96.31

Table 5: Dielectric constant values of 2 mol % KAPT

	ε_r for various frequencies				
Temp ℃	100HZ	1KHZ	10KHZ	100KHZ	1MHZ
150	1331.47	1256.56	1176.92	1004.32	474.23
140	1265.65	1195.56	1004.94	994.99	452.15
130	1194.94	956.56	906.36	852.54	434.19
120	956.56	856.72	814.95	756.43	395.95
110	852.72	744.42	718.19	694.95	310.17
100	794.45	694.94	624.32	545.54	286.18
90	695.55	595.95	554.32	495.95	254.94
80	556.96	496.72	416.72	410.96	198.15
70	506.88	410.39	398.15	364.15	174.95
60	454.94	372.49	316.17	298.99	159.45
50	414.18	319.79	298.15	210.15	131.42

with total weight loss at about above 485 °C of 38.61% which shows that one molecule of water is lost.

CONCLUSION

Tryptophan doped KAP single crystals were grown from the aqueous solution using slow evaporation solution growth technique. X-ray diffraction results proved that the crystals belong to orthorhombic system. The decomposition patterns of KAPT are proved by DSCTGA analysis. The FTIR study confirmed the presence of functional groups of the amino acid and KAP. The optical spectra revealed the transmittance of the single crystals. The aromatic ring may be substituted by alkyl, acyl, nitryl, acetyl and amino groups in different o and m positions and the effect of substituent's on the dielectric and non linear optic behaviour may be studied.

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