INVESTIGATIONS ON THE GROWTH, OPTICAL, SPECTRAL, THERMAL AND DIELECTRIC STUDIES OF EDTA DOPED POTASSIUM ACID PHTHALATE CRYSTAL

J. Bhuvana[1], N. Prabha[2]

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Abstract

Potassium acid Phthalate with EDTA (KAPE) crystals were allowed to grow for about three to four weeks at room temperature without disturbing the vessels containing solutions and were harvested. Optical absorption studies revealed that the doped crystals possess very low absorption in the entire visible region. The presence of functional groups in the crystal lattice has been determined qualitatively by FTIR analysis. The thermal stability was evaluated by TG-DSC analysis. The dielectric constant has been studied as a function of frequency for the doped crystals. Grown crystals were characterized by single crystal XRD and confirmed that the crystal belongs to orthorhombic system.

Keywords: Potassium acid phthalate; EDTA; Solution growth; UV; FTIR; Optical Imaging Microscopy; TG-DSC; XRD

[1]Assistant Professor, Dept.of Chemistry, A.D.M. College for Women, Nagapattinam, Tamil Nadu, India. (Affiliated to Bharathidasan University, Tiruchirappalli)
[2]Assistant Professor, Dept.of Chemistry, A.D.M. College for Women, Nagapattinam, Tamil Nadu, India. (Affiliated to Bharathidasan University, Tiruchirappalli)

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1. Introduction

The evolution of our knowledge of crystal growth requires not only scientific understanding, but also the driving force of applied technology which so often provides a significant influence in highlighting our lack of scientific knowledge and the need for a more refined science and indeed the development of new concepts. Their ever-increasing application of semi conductor based electronics creates an enormous demand for high quality semi conducting, ferro electric, piezo electric, oxide single crystals[1].Non linear optics is essentially concerned with the study of phenomena that result from field induced modifications in the optical properties of the materials [2].The large nonlinear optical effects found in organic crystals make them attractive for applications in frequency conversion and optical processing [3]. NLO materials play an important role in the field of fibre optic communications and optic signal processing. In the last two decades, extensive research has shown that organic crystals exhibit nonlinear optical efficiencies which have the orders of magnitude higher than those of inorganic materials [4,5].

In recent years much attention has been paid to semi-organic NLO materials and many studies have been reported [6-9].There are four chemical units of the formula K ($C_6H_4COOHCOO$), in unit cell of KAP. It has platelet morphology with a perfect cleavage along the (0 1 0) plane. The crystals have excellent physical properties and have a good record for long term stability in devices [10-12]. The aim of present work is to study the influence of dopants on the morphology and properties of KAP single crystals. Hence the effect of dopants i.e. EDTA, their structural, optical, spectral, mechanical, and dielectric properties has been studied.

Experimental

KAP salt was dissolved gradually in deionised water until a saturated solution was obtained and kept in four different beakers. The calculated amount of 1 mol %, 2 mol %, 6 mol % and 12 mol % of EDTA was added to the solution using magnetic stirrer. Then the solution was filtered and crystallization was allowed to take place by slow evaporation under room temperature.

Potassium acid Phthalate with EDTA (KAPE) crystals were allowed to grow for about three to four weeks at room temperature without disturbing the vessels containing solutions and were harvested. The harvested crystals of 1 mol % KAPE were shown in the fig.1, 2 mol % KAPE were showninthefig.2,6 mol % KAPE were shown in the fig 3, 12 mol % KAPE were shown in fig 4 and the size of the single crystals are 2 cm, 2.8. cm, 3.5 cm and 4.8 cm respectively.

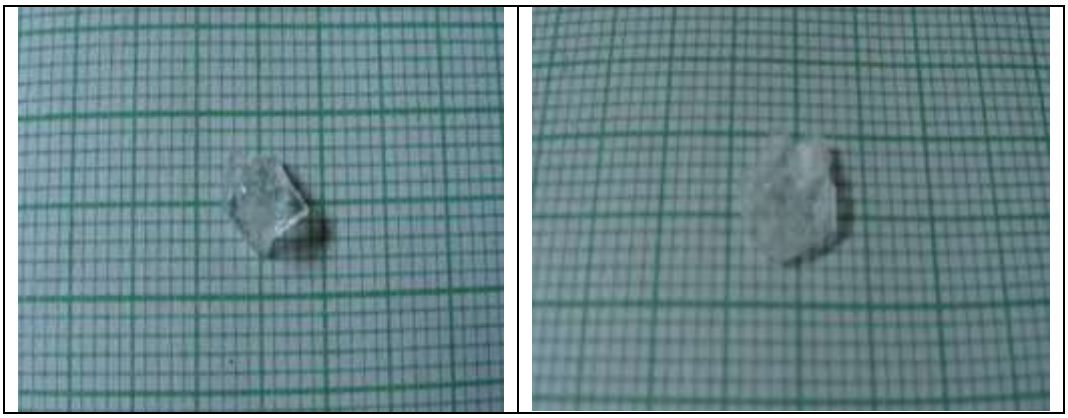


Fig.1 1 mol % KAPEFig.2 2 mol % KAPE

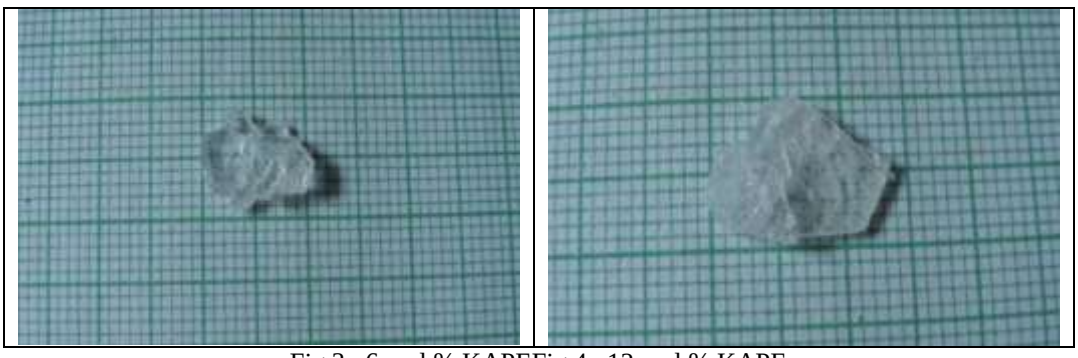


Fig.3 6 mol % KAPEFig.4 12 mol % KAPE

Characterisation Studies of Kape Crystal
Photography with Optical Imaging Microscopy

The morphology of the crystals was taken by using LX 400 Optical Microscopy and the photographs of 1 mol % KAPE, 2 mol % KAPE, 6 mol % KAPE and 12 mol % KAPE shown in Fig 5 to 8 respectively. The size of the crystals in Optical Imaging Microscopy is 99.64µm, 99.92µm, 100.78µm and 101.45µm.

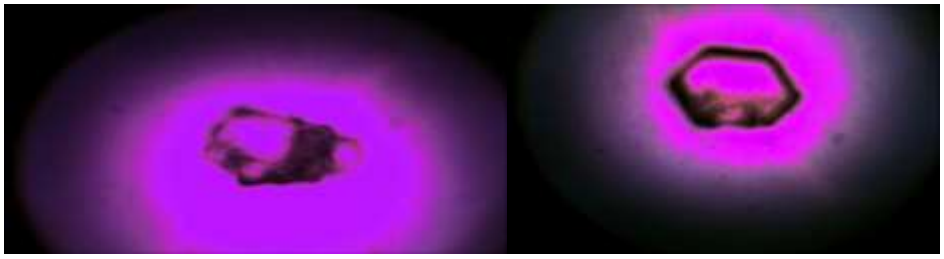


Fig.5 1 mol % KAPEFig.6 2 mol % KAPE

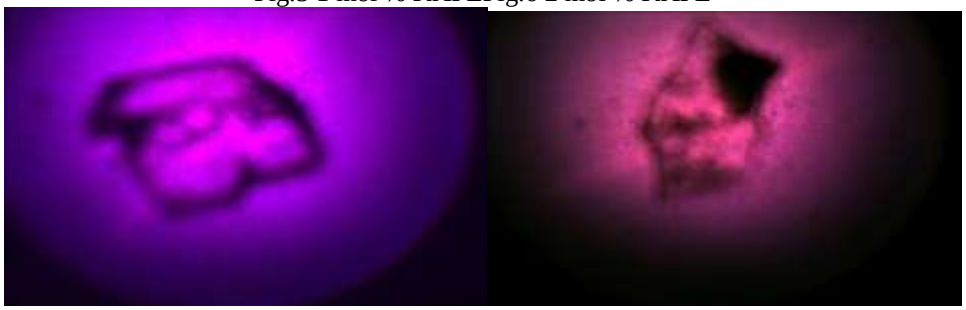


Fig.7 6 mol % KAPEFig .8 12 mol % KAPE

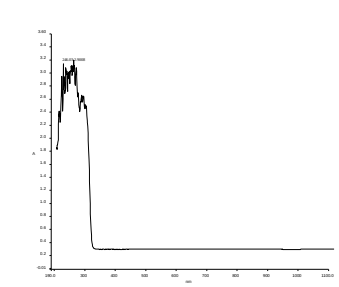
UV Spectral Analysis

The UV spectrum of KAP doped EDTA at four different concentrations (1 mol %, 2 mol %, 6 mol % and 12 mol %) were carried out using a double beam spectrophotometer in the range of 200nm-1100nm and shown in fig 9 to 12 respectively.

Table 1 Observed λ_{max} values of KAPE

1 mol % KAPE	2 mol % KAPE	6 mol % KAPE	12 mol %KAPE	Assignment
-	221.97	-		σ - σ*
246.03	-	248.79	236.07	π - π*
-	279.54	-	-	n -π*

In fig.9, the absorption at 246.03nm is due to π -π* transition represents the promotion of π electrons to an antibonding π orbital.In fig.10, two signals are obtained due to σ - σ* transition at 221.92nm and n-π*transition at 279.54nm. In fig.11, the observed λ_{max} value at 248.79 nm due to π -π* transition represents the promotion of π electrons to an antibonding π orbital.



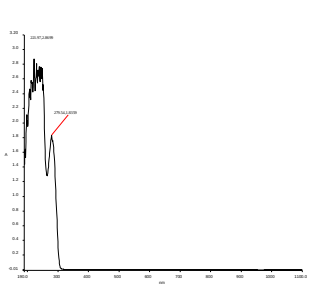
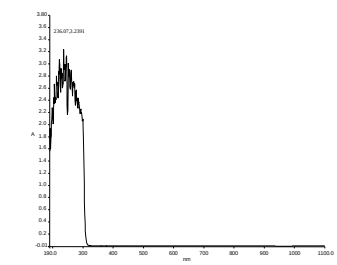


Fig.9 UV Spectrum of 1 mol % KAPE Fig.10 UV Spectrum of 2 mol % KAPE



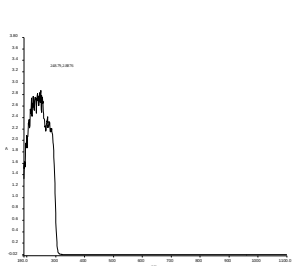
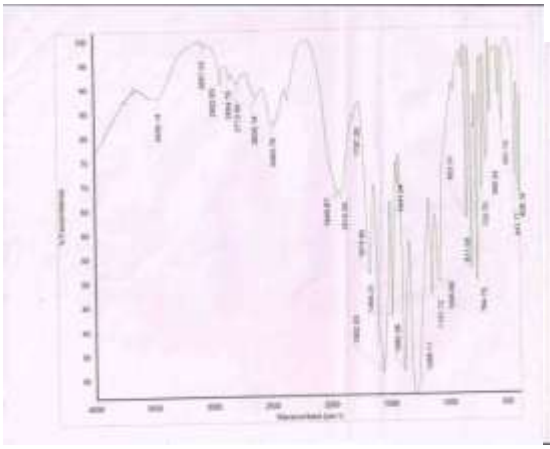


Fig.11 UV Spectrum of 6 mol % KAPE
Fig.12 UV Spectrum of 12 mol % KAPE

FTIR SPECTRAL ANALYSIS The FTIR spectra for KAPE at 4 different concentrations were recorded in the range of 4000 – 400 cm^{-1} and shown in fig.13 to 16 respectively.



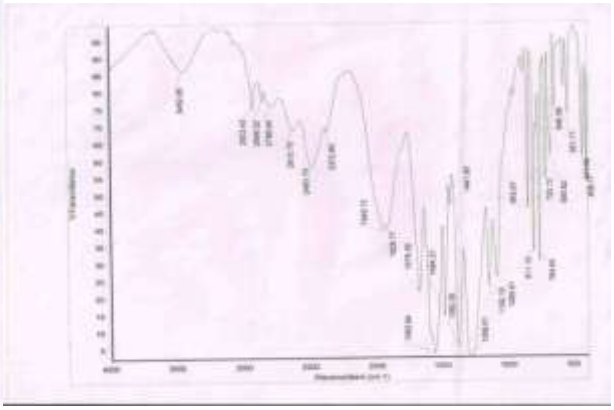
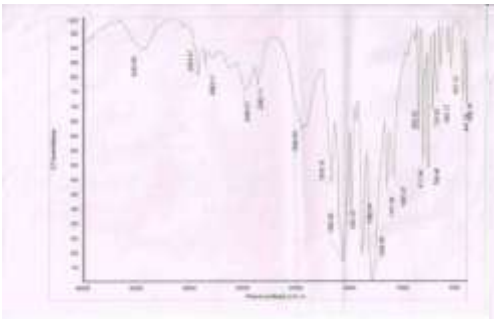


Fig.13 FTIR Spectrum of 1 mol % KAPE Fig.14 FTIR spectrum of 2 mol % KAPE

The presence of EDTA is confirmed by N – H stretching vibrations at 3430 cm^{-1}, 3452 cm-^{1}, 3432 cm^{-1} and 3452.05 cm^{-1} at1 mol %, 2 mol % , 6 mol % and 12 mol % KAPE. The intramolecular H bonded with C = O stretching appears at 2772 cm^{-1} and 2789 cm^{-1}. The peak occurs at 1382.38 cm^{-1}, 1382.39 cm^{-1}, 1382.34 cm^{-1} and 1382.51 cm^{-1} due to COO^{-} symmetric stretching vibrations. C-H out of plane bending occurs at 853.01 cm^{-1}, 853.07 cm^{-1}, 853.02 cm^{-1} and 853.08 cm^{-1} .



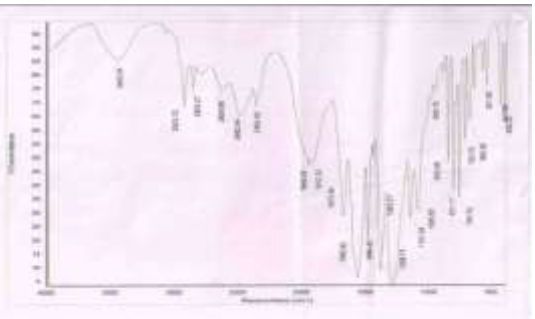


Fig.15FTIR Spectrum of 6 mol % KAPE Fig.16 FTIR spectrum of 12 mol % KAPE

Table.2 Infrared Absorption Frequencies of KAPE Crystal

Wave number cm^{-1}				
1 mol % KAPE	**2 mol % KAPE**	**6 mol % KAPE**	**12 mol % KAPE**	**Assignment**
3430	3452	3432	3452.05	N-H stretching vibration
2922	2923	2923	2923.72	C-H asymmetric and symmetric vibrations
2772	2789	-	-	Intra molecular H bonding with C = O
2483.79	2483.75	2482.51	2482.44	Overtones and combination of OH in plane bending and C-O stretching vibration
1675.85	1676.39	1676.16	1675.89	C=O stretching
1484.31	1484.21	1484.33	1484.40	C-H in plane bending
1382.38	1382.39	1382.34	1382.51	COO^- symmetric stretching
1151.72	1152.15	1151.92	1151.93	C- H in plane ring bending
853.01	853.07	853.02	853.08	C-H out of plane bending
720.70	720.72	720.63	720.75	N-H wagging and twisting

DSC AND TGA ANALYSIS

In order to identify the thermal stability, purity and crystalline nature of solution grown KAPE were subjected to thermal analysis. These studies were performed using thermal analyzer in the temperature range of 0°C to 600°C.The TG-DSC curves of KAPE at four different proportions shown in fig.17 to 20 respectively.

For 1 mol %, 2 mol %, 6 mol % and 12 mol % of KAPE, there is a sharp weight loss at 289.15°C, 280°C, 282°C and 285.71°C which corresponds to about 40.13%, 42%, 40% and 39.42%. This confirms the decomposition of the sample. In four different proportions of KAP doped EDTA, there is an single weight loss at 325°C with a total weight loss at about above 485°C of mass 40.13% which also shows that one molecule of water is lost.

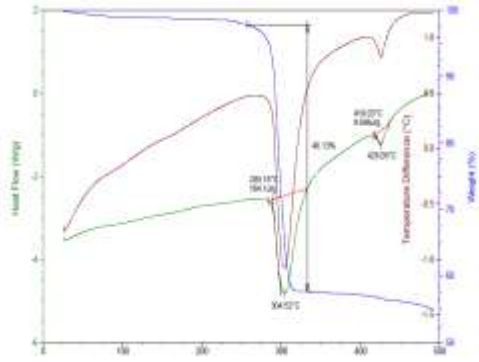


Fig.17 TGA – DSC of 1 mol % KAPE

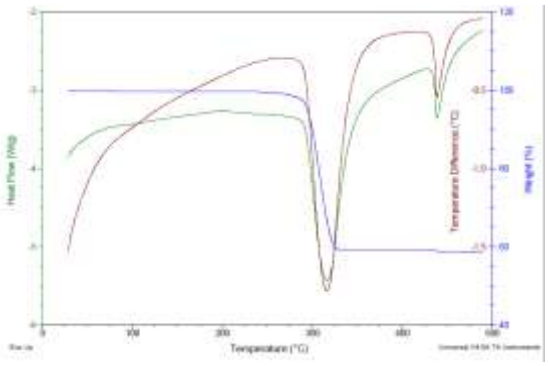
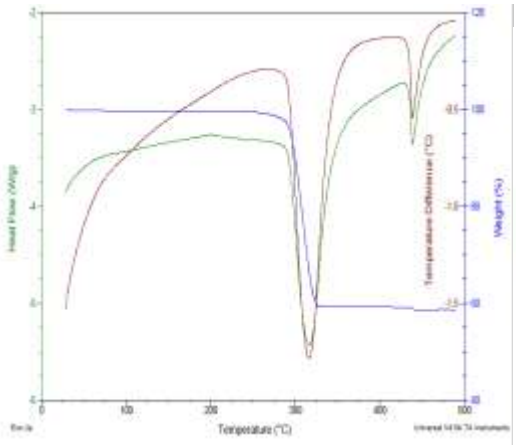


Fig.18 TGA-DSC of 2 mol % KAPE



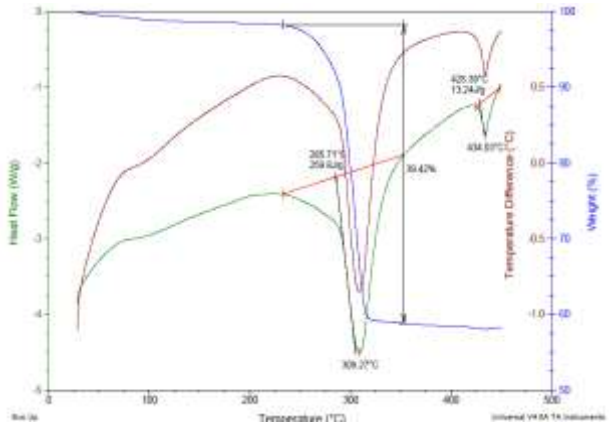


Fig.19 TGA – DSC of 6 mol % KAPEFig.20 TGA – DSC of 12 mol % KAPE

Conductivity Studies

Dielectric measurement is one of the useful methods for characterisation of electrical response in crystalline and ceramic materials. Single crystals of EDTA doped KAP cut in the rectangular specimen were subjected to dielectric studies. The dielectric constant and conductivity were calculated for 1 mol % KAPE, 2 mol % KAPE, 6 mol % KAPE and 12 mol % KAPE and tabulated in the table.3 to 10 respectively.

In general, Dielectric constant ε_r values increase when temperature increases at all frequencies for KAP crystals. Dielectric constant decreases when frequency increases.

AC conductivity values σ_{Ac} also increase when temperature increases at all frequencies for KAP crystals. In general, conductivity increases when frequency increases.

The increase in electrical parameters with increase in temperature may be due to the temperature dependence of the proton transport which inturn depends on the thermally generated defects. Graphs were drawn connecting ε_r Vs temperature and σ_{Ac}Vs temperature were shown in fig.21 to 28.

Table.3 Dielectric Constant Values of 1 mol % KAPE

Temp ℃	ε_r for various frequencies				
	100HZ	**1KHZ**	**10KHZ**	**100KHZ**	**1MHZ**
150	1278.23	1172.65	1004.64	999.98	380.41
140	1194.94	1004.65	956.15	856.96	354.65
130	956.68	910.98	856.65	756.45	332.19
120	872.16	799.72	749.19	694.95	304.46
110	764.64	688.15	594.64	545.74	256.98
100	659.54	543.72	432.15	400.19	222.55
90	546.46	438.15	349.72	310.19	198.19
80	494.32	382.44	310.54	254.65	174.45
70	454.65	310.15	298.15	210.96	156.15

Table.4 AC Conductivity Values of 1 mol % KAPE

Temp ℃	σ_{AC} x 10^6 for various frequencies				
	100HZ	**1KHZ**	**10KHZ**	**100KHZ**	**1MHZ**
150	4.8916	10.55	92.15	350	541.89
140	4.64	9.16	90.14	320.16	500.15
130	3.98	7.72	88.01	288.18	488.19
120	3.16	6.54	74.72	220.96	384.15
110	2.99	5.64	60.54	199.19	294.78
100	2.18	4.48	51.15	160.65	210.18
90	1.95	3.94	40.72	110.15	190.44
80	1.75	3.1	32.16	88.94	176.54
70	1.15	2.18	21.35	54.15	124.64
60	0.94	1.98	12.14	29.15	99.15
50	0.4128	1.08	4.19	11.15	86.281

Table .5 Dielectric Constant Values of 2 mol % KAPE

Temp ℃	ε_r for various frequencies				
	100HZ	**1KHZ**	**10KHZ**	**100KHZ**	**1MHZ**
150	1397.18	1219.24	1118.56	998.14	414.82
140	1254.55	1187.43	1001.15	872.64	398.19
130	1194.96	1009.15	933.37	810.94	372.43
120	1007.65	986.19	843.47	754.55	316.72
110	956.96	884.54	754.55	699.16	296.55
100	872.93	743.63	634.19	514.72	254.54
90	779.64	694.94	543.72	439.15	219.28
80	642.32	554.72	436.54	410.16	206.15
70	549.65	432.19	394.54	343.72	199.19
60	498.94	334.15	315.19	290.15	192.72
50	413.89	298.18	254.15	210.24	189.19

Table.6 AC Conductivity values of 2 mol % KAPE

Temp ℃	ε_r for various frequencies				
	100HZ	**1KHZ**	**10KHZ**	**100KHZ**	**1MHZ**
150	1452.37	1319.72	1209.16	1172.15	481.32
140	1355.55	1215.64	1196.72	1004.46	464.64
130	1246.37	1159.15	999.19	916.55	415.54
120	1194.46	992.64	856.45	804.95	398.72
110	1001.54	846.46	772.19	702.18	356.55
100	986.77	772.49	669.15	616.95	316.72
90	864.39	694.46	543.72	524.75	298.43
80	743.55	543.44	434.39	399.15	274.55
70	669.19	444.72	344.55	334.43	262.98
60	544.44	394.45	310.19	290.15	254.95
50	474.89	310.19	246.56	241.15	234.58

Table.7 Dielectric Constant Values of 6 mol % KAPE

Temp ℃	ε_r for various frequencies				
	100HZ	**1KHZ**	**10KHZ**	**100KHZ**	**1MHZ**
150	5.2438	12.15	93.18	312	621.28
140	4.44	11.54	88.15	300.14	588.18
130	3.8	10.58	74.19	260.49	510.6
120	2.54	9.72	59.64	200.14	486.15
110	2.18	8.64	48.94	185.54	386.18
100	1.95	7.1	36.45	134.13	294.34
90	1.66	6.15	25.16	99.15	210.18
80	1.38	4.98	19.18	81.16	184.54
70	1.18	3.19	11.54	64.68	140.32
60	0.99	2.28	8.72	32.19	112.15
50	0.5326	1.1972	4.19	10.16	94.181

Table.8 AC Conductivity values of 6 mol % KAPE

Temp ℃	ε_r for various frequencies				
	100HZ	**1KHZ**	**10KHZ**	**100KHZ**	**1MHZ**
150	7.8621	16.54	99.15	390	781.18
140	6.6672	15.94	90.16	340.64	700.18
130	5.43	13.22	80.19	300.92	680.19
120	4.48	11.1	71.18	284.64	566.49
110	4.16	9.84	64.64	100.18	482.18
100	3.88	8.16	59.65	165.18	410.16
90	3.16	7.72	49.64	148.94	382.45
80	2.24	6.54	38.94	100.49	310.94
70	1.99	5.16	27.64	54.72	260.42
60	1.04	3.98	19.18	39.94	220.18
50	0.9128	2.43	7.74	21.18	189.18

Table .9 Dielectric Constant Values of 12 mol % KAPE

Temp ℃	ε_r for various frequencies				
	100HZ	**1KHZ**	**10KHZ**	**100KHZ**	**1MHZ**
150	1571.98	1417.72	1319.54	1215.15	521.31
140	1364.46	1256.54	1192.64	1124.19	496.96
130	1172.72	1132.16	956.74	901.54	454.54
120	956.56	945.77	856.56	826.72	432.16
110	889.74	846.19	794.55	746.18	421.56
100	746.55	719.28	664.99	619.15	401.54
90	694.15	626.68	554.72	524.28	384.63
80	615.74	595.43	499.46	415.19	358.19
70	545.54	510.15	410.15	372.49	344.72
60	524.64	486.72	386.19	348.15	328.15

50	514.87	410.16	324.72	298.15	318.34

X-Ray Diffraction Studies

The single crystal X- ray diffraction analysis on KAPE single crystals 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 the different proportions of KAPE are given in Table 11. The XRD analysis have confirmed that the incorporation of chelating agent EDTA in the KAP crystal lattice.

Table 10 Crystallographic Parameters of KAPE

Sl.No	Parameters	1 mol % KAPE	2 mol % KAPE	6 mol % KAPE	12 mol % KAPE
1.	a	6.45	6.48	6.52	6.55
2.	b	9.60	9.63	9.68	9.78
3.	c	13.25	13.32	13.42	13.46
4.	Volume	821 A°	831 A°	847 A°	862 A°

Conclusion

EDTA doped KAP single crystals at four different proportions were grown from the aqueous solutions using slow evaporation solution growth technique. UV-Vis, FTIR, X-ray diffraction studies confirmed the presence of EDTA in KAP. The decomposition pattern of KAPE proved by TGA-DSC analysis. The dielectric constant and AC conductivity studies showed that EDTA doping change the dielectric behaviour of KAP crystal significantly.

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