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THERMAL ANALYSIS, EFFECT OF DOPANTS, SPECTRAL CHARACTERISATION AND GROWTH ASPECTS OF KAP CRYSTALS

G. Vasudevan[1], *P. AnbuSrinivasan*[1], *G. Madhurambal*[2] *and S. C. Mojumdar*[3,4*]

[1]Department of Chemistry, A.V.C. College, Mayiladuthurai, Tamilnadu, India
[2]Department of Chemistry, ADM College, Nagapattinam, Tamilnadu, India
[3]Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, Toronto ON, M5S 3E5, Canada
[4]Department of Engineering University of New Brunswick, Saint John, NB, E2L 4L5, Canada

Potassium acid phthalate (KAP) which is also known as potassium hydrogen phthalate ($KC_8H_5O_4$), a semi-organic compound was grown from its aqueous solution only by slow evaporation method at room temperature. The effect of metallic salts $HgCl_2$ and $PbCl_2$ as dopants in the growth aspects, thermal properties and SHG efficiency of KAP were determined using UV-VIS, FTIR spectral studies, thermal (TG and DTA) analysis and NLO test. There is only one significant mass loss step on TG curve of pure and doped KAP crystal. DTA curve exhibit a higher peak temperature in case of doped KAP crystal compared to those of pure KAP crystals.

Keywords: *effect of dopants, $HgCl_2$, KAP, $PbCl_2$ spectral characterization, SHG efficiency, thermal analysis*

Introduction

The habitual morphology of the potassium acid phthalate (KAP) crystal has 14 natural growth faces with dominating (010) face [1]. Since the (010) face is more suitable for any surface morphological studies, a number of crystal growth studies have been made on this material in recent years. Also KAP is used as an analyser material in X-ray spectroscopy [2]. Its electro-optical and non-linear optical properties were also reported [3]. Enhancement of metastable zone width for solution growth of potassium acid phthalate was also reported [4]. In recent years, considerable effort has been taken for the growth of high quality organic crystals by simple solution technique using slow evaporation method at room temperature [5, 6]. Various organic-inorganic materials were developed and studied to improve the properties of inorganic materials. Thermal, spectral and optical analyses are very useful techniques to various materials characterization [7–42]. This work is aimed at the characterization of KAP and $HgCl_2$ and $PbCl_2$ doped KAP crystals using thermal, spectral and optical analyses.

Experimental

Measurements

The solubility of KAP analar sample was determined for different temperatures by gravimetric method in triply distilled water. A plot of solubility of KAP *vs.* temperature (solubility diagram) indicating its increase in solubility with temperature is given in Fig. 1.

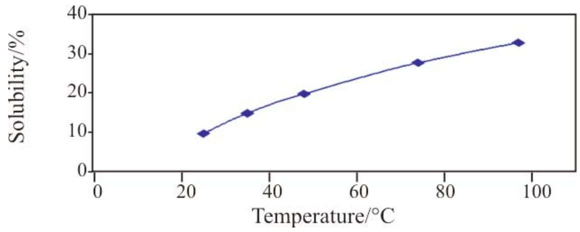

Fig. 1 Solubility diagram of pure KAP

After solubility determination studies, pure and 2 mole% of $HgCl_2$, $PbCl_2$ added KAP solutions were taken in three similar beakers at 30°C (room temperature) and kept undisturbed by covering with a thick sheet of paper for controlled slow evaporation. Good quality crystals of pure and $HgCl_2$, $PbCl_2$ doped KAP were obtained in a few days. They were carefully collected and subjected to UV-Vis and FTIR spectral studies, thermal analysis and NLO test.

UV-Vis spectral studies were carried out on a Lambda 35 UV-Vis spectrophotometer.

The FTIR spectral studies of pure and doped KAP crystals were performed on an AVATAR 330 FTIR spectrophotometer using the KBr pelletting technique.

Thermal analysis was performed between 25 and 450°C at a heating rate of 20°C min^{-1} in N_2 atmo-

* Author for correspondence: subhash.mojumdar@utoronto.ca

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

sphere on a SDT Q600 TA Instruments thermal analyzer.

Results and discussion

UV – visible spectral analysis

UV-visible spectral study is a useful tool to determine the transparency, which is an important requirement for a material to be optically active [43]. Pure and $HgCl_2$, $PbCl_2$ doped crystals were subjected to UV-Vis spectral studies using Lambda 35 UV-Vis spectrophotometer to determine their percentage of transparency and the recorded spectra are shown in Figs 2, 3 and 4. It is evident from the spectrum that pure KAP has about 8.5% transparency, KAP doped with $HgCl_2$ has about 12% transparency and KAP doped with $PbCl_2$ has about 50%.

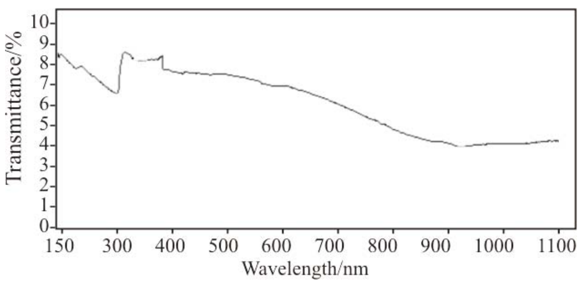

Fig. 2 UV-Vis spectrum of pure KAP

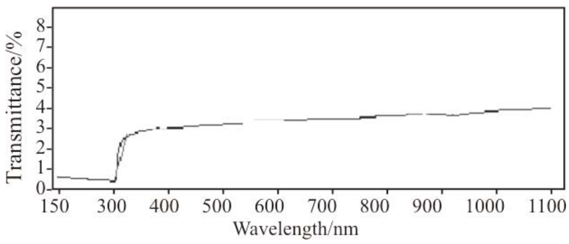

Fig. 3 UV-Vis spectrum of KAP doped with $HgCl_2$

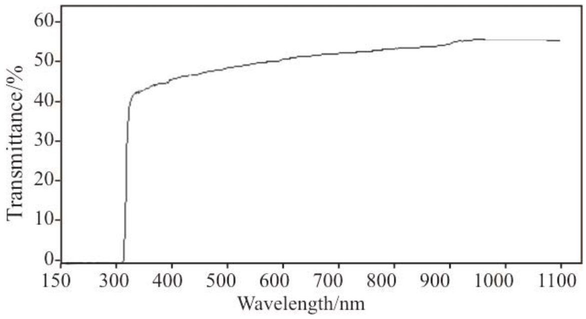

Fig. 4 UV-Vis Spectrum of KAP doped with $PbCl_2$

FTIR spectral studies

Infra–red spectrum is an important record, which gives sufficient information about the structure of a compound. In this technique almost all functional groups in a molecule absorb characteristically within a definite range of frequency [44]. The range 4000–400 cm^{-1} is of prime importance for the study of an organic compound by spectral analysis [45]. Pure KAP and doped KAP crystals show characteristic absorption bands. From the Table 1, it is evident that the percentage of transmission for doped crystals is higher than that of pure KAP. FTIR spectra of pure KAP and KAP doped with $HgCl_2$ and $PbCl_2$ are shown in Figs 5, 6 and 7.

Thermal studies

In order to identify the thermal stability, purity and crystalline nature of solution grown pure KAP and $HgCl_2$ and $PbCl_2$ doped KAP crystals, they were subjected to thermal analysis. In pure KAP and doped KAP crystals mass loss is noted on TG curve mainly in one major step indicating similar decomposition.

In DTA, endothermic peak is obtained for doped KAP crystals at a little bit higher temperature (311.71°C for $HgCl_2$ doped KAP and 309.34°C for

Table 1 FTIR spectral results of pure and $HgCl_2$ and $PbCl_2$ doped KAP crystals

SI no.	Vibration	Transmission/%		
		Pure KAP	2% $HgCl_2$	2% $PbCl_2$
1	C=O symmetric stretching at 1565 cm^{-1}	3.33	10.02	3.36
2	C=C ring stretching at 1485 cm^{-1}	18.08	26.75	24.26
3	C=O symmetric stretching at 383 cm^{-1}	7.32	14.95	9.26
4	C=C stretching at 1280 cm^{-1}	4.66	11.44	8.8
5	C–C=O stretching at 1090 cm^{-1}	13.08	19.45	12.06
6	C–H out of plane bending at 850 cm^{-1}	49.54	38.83	60.68
7	O–H out of plane bending at 720 cm^{-1}	46.32	47.46	42.54
8	C–C–C out of plane ring deformation at 582 cm^{-1}	68.53	65.32	57.51

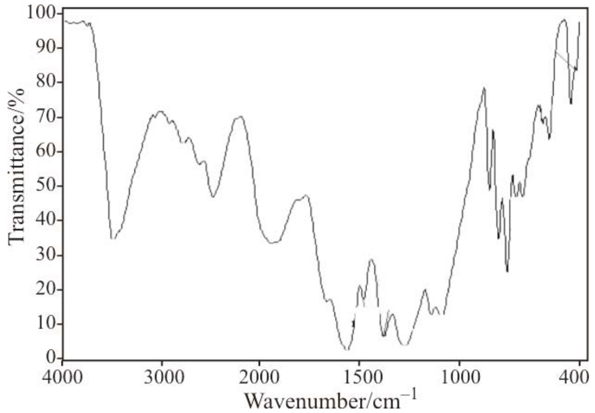

Fig. 5 FTIR Spectrum of pure KAP

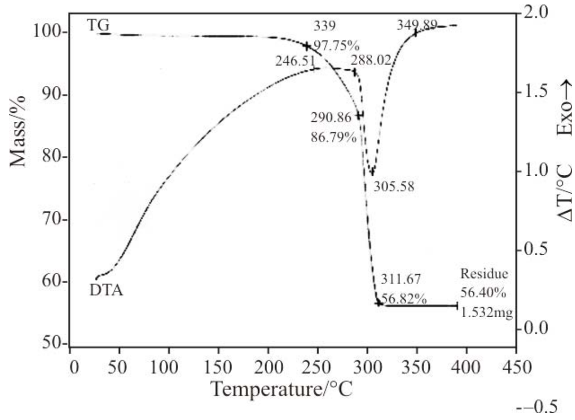

Fig. 8 TG and DTA curves of pure KAP

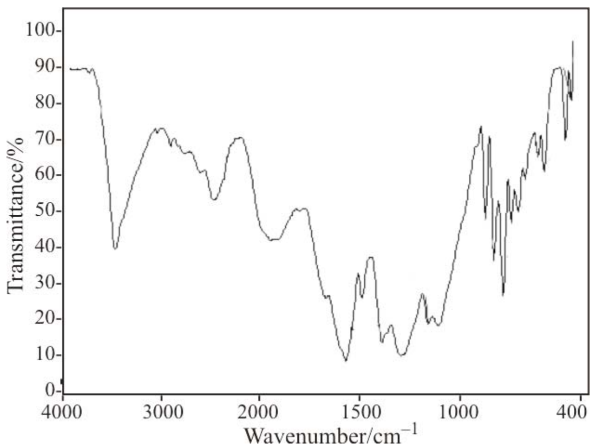

Fig. 6 FTIR Spectrum of KAP doped with $HgCl_2$

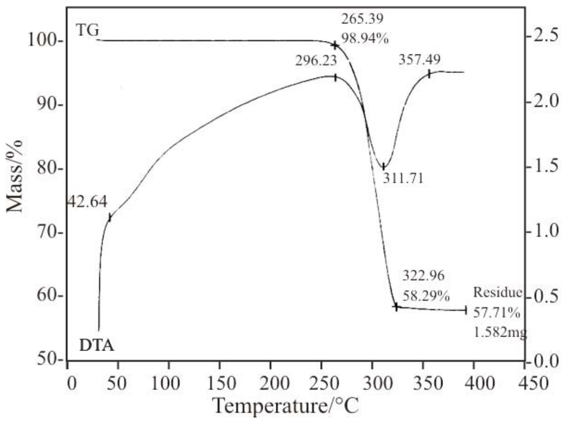

Fig. 9 TG and DTA curves of KAP doped with $HgCl_2$

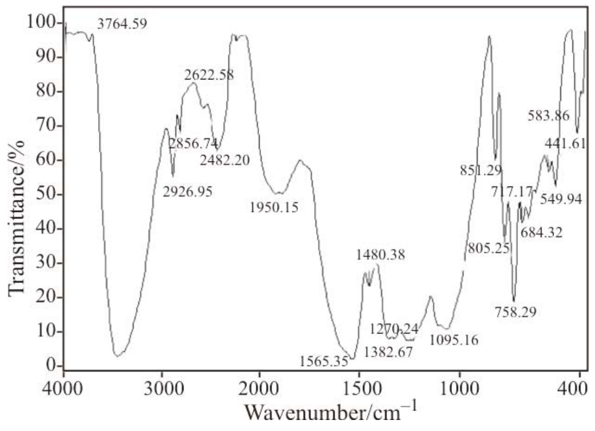

Fig. 7 FTIR spectrum of KAP doped with $PbCl_2$

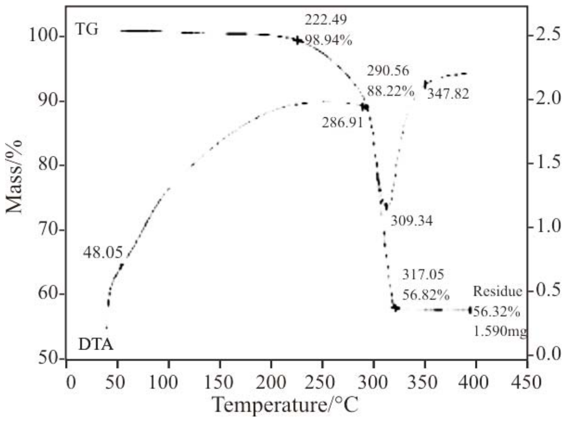

Fig. 10 TG and DTA curves of KAP doped with $PbCl_2$

$PbCl_2$ doped KAP) compared to the pure KAP crystal (305.58°C) indicating that the decomposition peak temperature slightly increases. The TG and DTA curves of solution grown pure KAP and KAP doped with $HgCl_2$ and $PbCl_2$ are shown in Figs 8, 9 and 10 and they support the single crystalline nature of grown crystals. This further supports that the DTA peak temperature is shifted to higher temperature by the addition of dopants $HgCl_2$ and $PbCl_2$.

NLO property

The fundamental beam 1064 nm from Nd:YAG laser is used to test second harmonic generation (SHG). SHG efficiency of KAP is 44 whereas that of $HgCl_2$ and $PbCl_2$ doped crystals is 54 and 48, respectively. It is evident from the NLO test that the SHG efficiency of KAP gets enhanced by the addition of dopants $HgCl_2$ and $PbCl_2$.

Conclusions

Good quality KAP and $HgCl_2$, $PbCl_2$ doped KAP crystals were grown by solution technique using slow evaporation method at room temperature. The optical transparency of KAP gets altered by the addition of $HgCl_2$ and $PbCl_2$. This is evident from the fact that the SHG efficiency of doped crystals is higher. As the SHG efficiency plays an important role in the instrumentation involving electro-optic materials, the doped crystals may be used for suitable electro-optic applications and may be used to modify the optic and electro-optic properties of KAP crystals. The thermal stability of KAP crystal was also influenced by the addition of $HgCl_2$ and $PbCl_2$. Doping may enhance the optical utility of KAP crystal due to the increase in thermal stability.

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