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Effect of dopant on the characterization of KAP crystal

Thermal and spectral analysis

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Abstract Potassium Hydrogen Phthalate also known as Potassium Acid phthalate (KAP) has 14 natural growth faces with dominating (010) face. As 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. Here this semi organic crystal was grown by Slow Evaporation Solution Growth Technique. The effect of ammonium sulphate as dopant on the characteristic properties of KAP crystal was studied by thermal and spectral analysis.

Keywords Ammonium sulphate · Effect of dopant · KAP · TG-DTA · Spectral characterization

Introduction

The enhancement of metastable zone width for solution growth of potassium acid phthalate, its electro-optical and non-linear optical properties was reported [1, 2]. Several organic inorganic materials were developed and studied to improve the properties of inorganic materials. Thermal, spectral, structural and optical studies are very useful techniques in the characterisation of various materials [3–39]. The effect of metallic salts $HgCl_2$ and $PbCl_2$ as dopants in the growth aspects, thermal properties and second harmonic generation (SHG) efficiency of KAP were determined and reported in [40]. A detailed investigation have been made on growth aspects of KAP and the effect of ammonium sulphate as dopant, using UV, FTIR spectral analyses and thermal studies in this study. The SHG efficiency of pure and ammonium sulphate-doped KAP were determined.

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Experimental

Solubility determination

The solubility of KAP sample was determined at different temperatures using gravimetric method in triply distilled water. The solubility diagram of KAP versus temperature is presented in Fig. 1 which shows the increase in solubility with temperature. Pure and 2 mol% of ammonium sulphate added KAP solutions were taken in two similar beakers at 30 °C (room temperature) and kept undisturbed by covering with a thick sheet of paper for controlled slow evaporation after solubility determination. Good quality crystals of pure and ammonium sulphate-doped KAP were obtained in a few days. The crystals were carefully collected and subjected to UV–Vis and FTIR spectral studies, NLO test and thermal analysis.

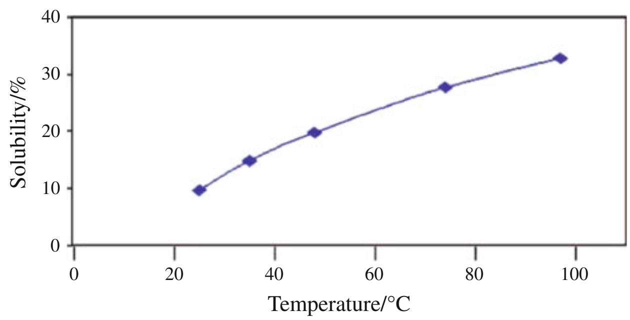

Fig. 1 Solubility diagram of pure KAP crystal

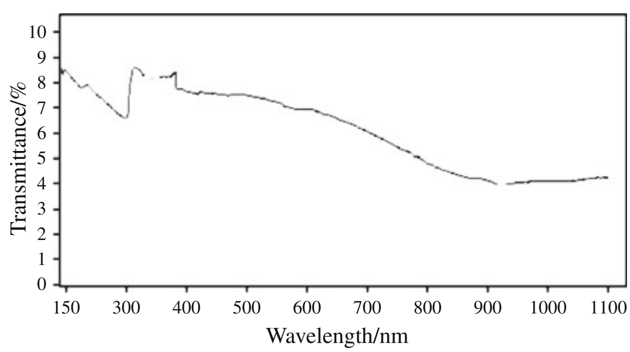

Fig. 2 UV–Vis spectrum of pure KAP crystal

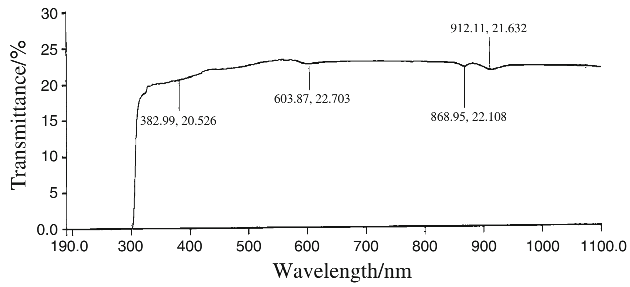

Fig. 3 UV–Vis spectrum of ammonium sulphate-doped KAP crystal

Measurements

Thermal analysis was carried out at 25–450 °C in N_2 atmosphere at a heating rate of 20 °C/min on a SDT Q600 thermal analyzer of TA Instruments.

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

UV–Vis spectral studies were performed on a Lambda 35 UV–Vis spectrophotometer.

Table 1 Characteristic FTIR spectral absorptions of pure KAP and ammonium sulphate-doped KAP crystals

Sl. no.	Vibration	Transmission/%	
		Pure KAP	2% Ammonium sulphate
1	C=O asymmetric stretching at 1565 cm^{-1}	3.33	7.36
2	C=C ring stretching at 1485 cm^{-1}	18.08	43.18
3	C–C stretching at 1280 cm^{-1}	4.66	30.73
4	C–C=O stretching at 1090 cm^{-1}	13.08	31.31
5	C–H out of plane bending at 850 cm^{-1}	49.54	75.26
6	O–H out of plane bending at 720 cm^{-1}	46.32	60.8

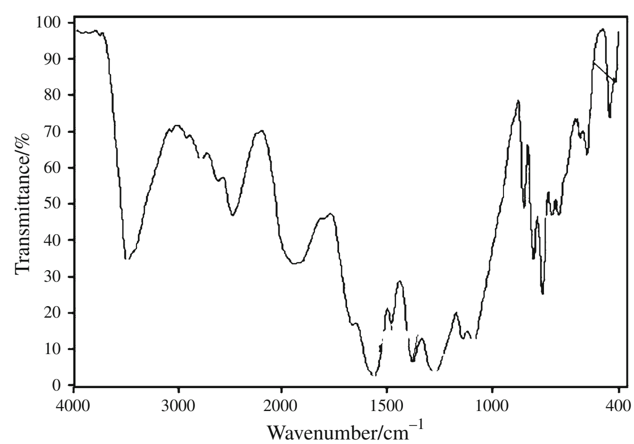

Fig. 4 FTIR Spectrum of pure KAP crystal

Results and discussion

UV–Vis spectral studies

UV–Vis spectral study is a very useful technique to determine the transparency, an important requirement for an optically active material [41]. Pure and ammonium sulphate-doped crystals were used to obtain UV–Vis spectra on a Lambda 35 UV–Vis spectrophotometer to determine their percentage of transparency and the recorded spectra are shown in Figs. 2 and 3. It is evident from the spectrum that pure KAP has about 8.5% transparency, whereas ammonium sulphate-doped KAP had nearly 20% transparency.

FTIR spectral analysis

FTIR spectra are very important records, which give sufficient information about the structure of various

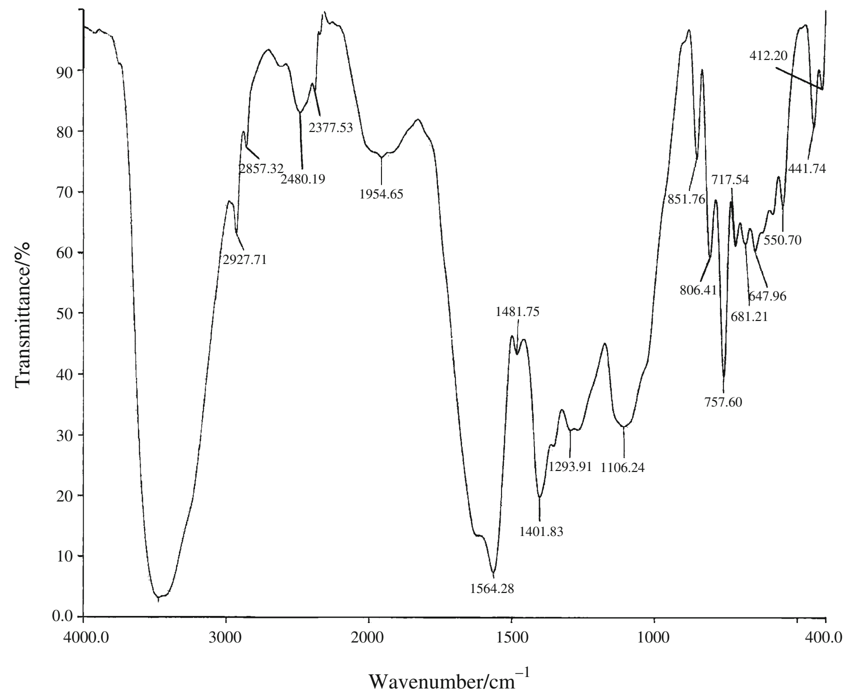

Fig. 5 FTIR spectrum of ammonium sulphate-doped KAP crystal

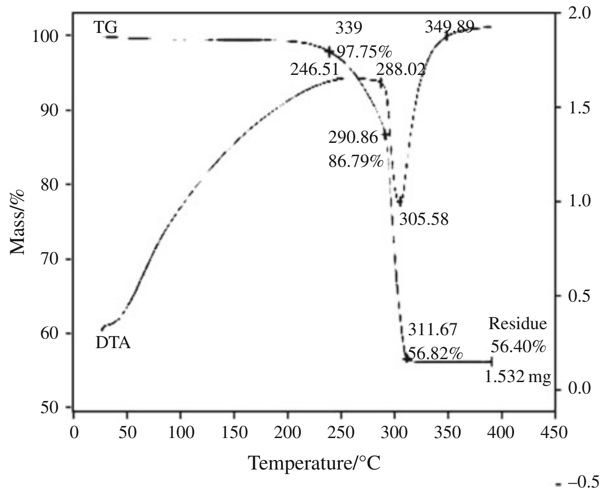

Fig. 6 TG and DTA curves of pure KAP crystal

compounds. Almost all functional groups in a molecule absorb characteristically within a definite range of frequency in this technique [42]. The range 4000–400 cm^{-1} is of most importance for the study of an organic compound by spectral analysis [43]. FTIR spectral studies of pure KAP and ammonium sulphate-doped KAP crystals show all the characteristic absorption, which is given in Table 1. FTIR spectra of pure KAP and ammonium sulphate-doped KAP are shown in Figs. 4 and 5. The percentage of transmission for doped crystal is higher than that for pure KAP.

TG and DTA studies

Solution grown pure KAP and ammonium sulphate-doped KAP crystals were subjected to thermal analysis to identify their thermal stability, purity and crystalline nature. In pure KAP and doped KAP crystals, mass loss is noted on TG curve mainly in one major step indicating similar decomposition. For pure KAP and ammonium sulphate-doped KAP, weight loss was noted on TG curves in the same range of temperature indicating similar decompositions. The TG and DTA curves are shown in Figs. 6 and 7. It is evident that the dopant does not have much influence on the thermal stability of KAP crystal. Thermal studies further support the single crystalline nature of grown crystals.

NLO property

The fundamental beam 1064 nm from Nd:YAG laser is used to test second harmonic generation (SHG) of pure KAP and ammonium sulphate-doped KAP crystals. SHG efficiency of pure KAP and ammonium sulphate-doped crystals is 44 and 54, respectively. It is confirmed by the NLO test that the SHG efficiency of KAP has enhanced by the addition of dopant ammonium sulphate.

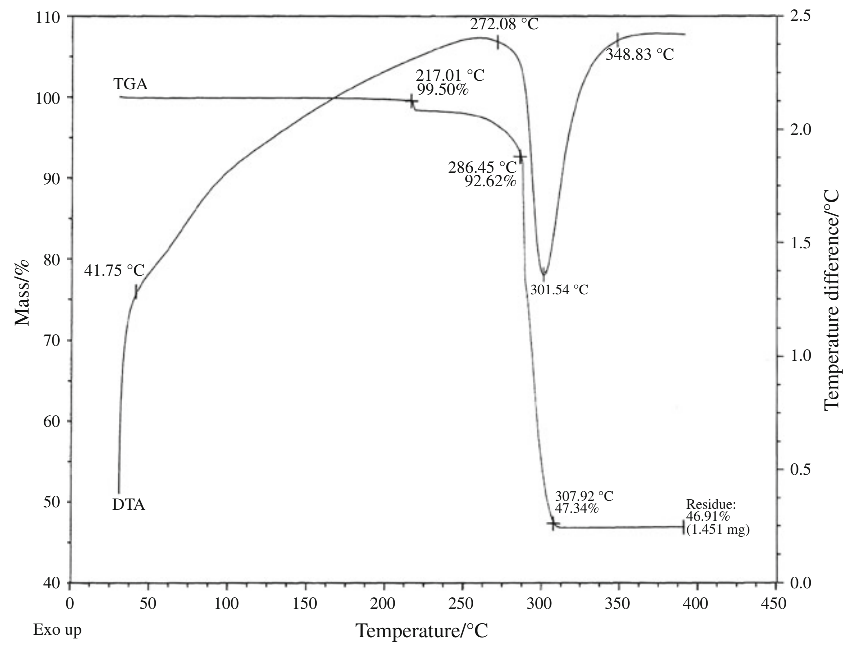

Fig. 7 TG and DTA curves of ammonium sulphate-doped KAP crystal

Conclusions

Pure KAP and ammonium sulphate-doped KAP crystal have been grown by the slow evaporation solution growth Technique. The UV–Visible spectral analysis gives evidence that ammonium sulphate-doped KAP crystal has higher transparency. The FTIR spectral studies support the characteristic absorptions of pure KAP and ammonium sulphate-doped KAP crystals. The dopant ammonium sulphate does not influence the thermal stability of KAP crystal. There is an appreciable enhancement in the SHG efficiency of doped crystal compared to pure KAP crystal. Thus, ammonium sulphate as dopant of KAP crystal enhances the optical utility of KAP crystal.

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