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Effect of anthracene doping on potassium hydrogen phthalate crystals

S. Meenakshisundaram · S. Parthiban ·
U. R. Pisipaty · G. Madhurambal · S. C. Mojumdar

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Abstract The influence of the highly fluorescent dopant, anthracene (over a concentration range from 5×10^{-4} to 1.2×10^{-2} mol dm^{-3}) on the nonlinear optical properties and fluorescence intensity of potassium hydrogen phthalate (KHP) single crystals grown at 30 °C by a slow evaporation solution growth technique (SEST) has been investigated. Powder XRD and FTIR spectral analyses confirm the slight distortion of the structure of crystal because of doping. UV–Visible study shows that the transparency is not affected much by the dopant. The SEM investigation reveals that KHP suffers from crack development. Thermal analysis indicates that there is no decomposition of the crystal up to the melting point. It is interesting to observe that additions of small quantity anthracene to KHP results in the enhancement of fluorescence intensity. The fluorescence intensity dependence on dopant concentration is observed. Interestingly, second harmonic generation (SHG) efficiency of KHP is dramatically improved by doping with small quantities of anthracene.

Keywords Organic dopants · Non-linear optical · Thermal analysis · XRD · KHP

Introduction

Potassium hydrogen phthalate (KHP) crystal is well known for its application in the production of crystal analyzer for long wave X-ray spectrometer [1, 2]. KHP possesses piezoelectric, pyroelectric, elastic and nonlinear optical properties [3–5]. It crystallizes in orthorhombic structure with space group Pca2_1 [6]. It has a platelet morphology with perfect cleavages along (010) plane. Recently, KHP crystals are used as substrates for the growth of highly oriented film of conjugated polymers with nonlinear optical susceptibility [7, 8]. KHP is chosen as model compound because of its well developed surface pattern on the (010) face consisting of high and very low growth steps which can be relatively easily observed by means of optical microscopy [9, 10]. KHP is used as a substrate for the deposition of thin films of non-linear optical (NLO) materials like urea with high mechanical stability [11].

Anthracene is one of the organic photoconductors [12–15] extensively investigated over five decades. It belongs to the monoclinic system and the electronic conduction of anthracene is due to free electrons and holes present in the crystal. It is reported that free carriers are generated when crystal is illuminated by light of wavelength about 400 nm [16–18] and hence it is active in the UV region of electromagnetic spectrum. The polynuclear aromatic hydrocarbons (PAHs) forming homogenous mixed crystals are known to exhibit

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S. Meenakshisundaram · S. Parthiban
Department of Chemistry, Annamalai University,
Annamalainagar, Tamil Nadu 608 002, India

U. R. Pisipaty
Department of Chemistry, SCSVMV University, Kanchipuram,
Tamil Nadu, India

G. Madhurambal
Department of Chemistry, ADM College for Women,
Nagapattinam, India

S. C. Mojumdar (✉)
Department of Chemical Engineering and Applied Chemistry,
University of Toronto, 200 College Street, Toronto,
ON M5S 3E5, Canada
e-mail: subhash.mojumdar@utoronto.ca; mojumdar@unbsj.ca;
scmojumdar@yahoo.com

S. C. Mojumdar
Department of Engineering, University of New Brunswick, Saint
John, NB E2L 4L5, Canada

excimer and exciplex emissions [19–21]. Such emissions are explained on the basis of intra and inter-molecular energy transfer processes [22, 23]. The highly fluorescent anthracene functioning as an efficient donor is reported to form charge transfer complex (CTC) with diethyl aniline acceptor in solution [20]. The formation of CTC between anthracene and other PAHs is also probable in crystalline state if the acceptors are selected properly. From this viewpoint, efforts have been focused on the preparation of multi-component mixed crystals and in studying their fluorescence characteristics. It was found that the crystalline naphthalene serves as good medium in which solid solution of anthracene and other PAHs could be prepared. Red shift in the fluorescence of naphthalene doped by anthracene has been reported [24]. SEM, thermal, spectral and X-ray analyses are very useful techniques for materials characterization. Therefore, many authors have used these techniques for various materials investigation [25–56]. This paper reports the growth and the effect of anthracene doping on the thermal, spectral, X-ray and optical properties of KHP crystals.

Experimental

Crystal growth

Potassium hydrogen phthalate (KHP) crystals were grown from high purity salt (EM). Solubility of KHP was maintained in the temperature range 30–35 °C and the growth solution was prepared according to the solubility data. A small quantity of dopant anthracene (SD fine) (0.0005–0.012 mol dm^{-3}) dissolved in DMSO was used for doping. The solution was stirred at 30 °C and slow evaporation method was used for the growth from aqueous solution. Studies follow the general trend that the growth rate of crystals in the presence of impurities always decreases with increase in impurity concentration. At high concentration of the dopants the adsorption film blocks the growth surface and inhibits the growth process. The growth promoting effect (GPE) of anthracene was high with a low dopant concentration (5×10^{-4} mol dm^{-3}). Photographs of pure and anthrancene doped KHP crystals are shown in Fig. 1. Quality of crystals is much better in the case of low doping.

Measurements

The powder X-ray diffraction was performed on a Philips Xpert Pro Triple-axis X-ray diffractometer. The samples were examined with Cu K_α radiation in the 2θ range from 10° to 70°. The XRD data is analysed by Rietveld method with RIETAN-2000.

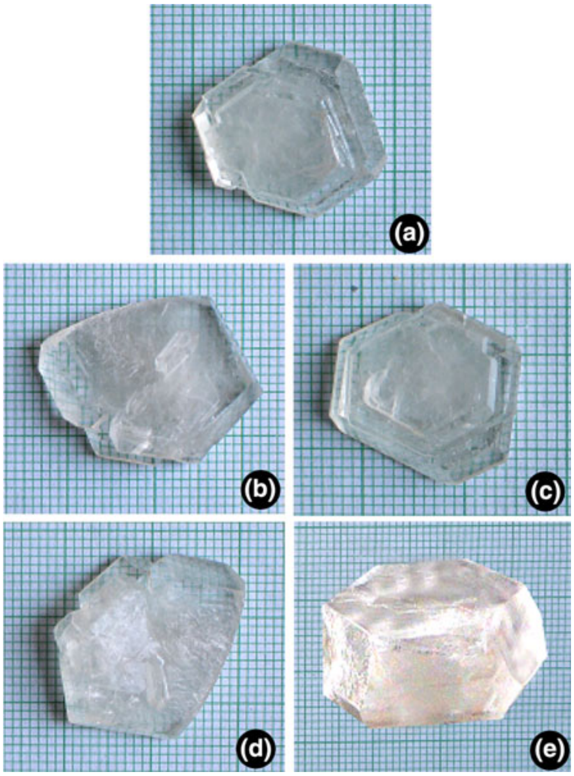

Fig. 1 Photographs of KHP crystals: **a** pure KHP and **b**–**e** KHP doped with various concentrations of anthracene: **b** 0.0005 mol dm^{-3}, **c** 0.0015 mol dm^{-3}, **d** 0.005 mol dm^{-3} and **e** 0.012 mol dm^{-3}

The FT-IR was recorded for both the doped and undoped specimens using AVATAR 330 FT-IR using KBr pellet technique in the range 500–4,000 cm^{-1}.

Morphologies of the samples were observed on a JEOL JSM 5610 LV scanning electron microscope.

The second harmonic generation (SHG) test on the crystals was performed by the Kurtz powder SHG method [57]. An Nd:YAG laser with modulated radiation of 1,064 nm was used as the optical source.

Fluorescence was measured using an ELICO fluorescence instrument.

The UV–visible absorption spectra were recorded on a Hitachi UV–visible spectrometer in the spectral range from 200 to 1,000 nm. TG-DTA analyses were carried out on a Universal SDT Q600 thermal analyser of TA Instruments at the heating rate 20 °C/min in nitrogen.

Results and discussion

X-ray diffractometry

XRD patterns of KHP crystals grown rapidly in anthracene added solution is compared with that of pure KHP crystal (Fig. 2). XRD profile of product is consistent with that of pure KHP crystal. No change in basic structure is observed. The XRD data is analysed with Rietveld method with RIETAN-2000. The lattice parameters are $a = 9.642$ Å, $b = 12.130$ Å, $c = 6.655$ Å, $\alpha = \beta = \gamma = 90°$. However, the relative intensities of the two patterns differ. The corresponding peak intensity ratio (I/I_o) of pure KHP is markedly different from (I'/I_o) of the doped specimen. The change in intensity pattern reveals the lattice distortion because of doping. The preferred orientations (110) of doped and pure samples remain the same. The crystallite sizes (D) of both pure and doped samples were calculated using Scherrer equation. The granularity of the crystals decreases from 37 to 25 nm by doping. It appears that anthracene doping inhibits the growth of the crystals.

FT-IR spectroscopy

The characteristic vibrational spectra of pure and anthracene doped KHP crystals are shown Fig. 3. FTIR spectra reveal that the KHP crystal has undergone considerable lattice distortion. Further, it appears that the distortion is concentration dependent. It has been reported that anthracene can form CTC with diethyl aniline [20] and polynuclear hydrocarbons [58]. XRD and FTIR studies reveal the lattice strain and as such a type of CTC formation in the present study is not entirely ruled out. This aspect has to be probed further.

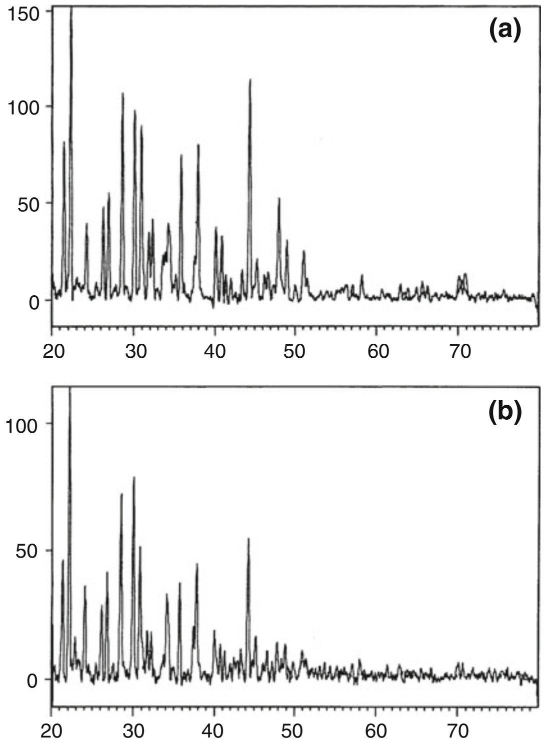

Fig. 2 Powder XRD of **a** pure and **b** 0.012 mol dm^{-3} anthracene doped KHP crystals

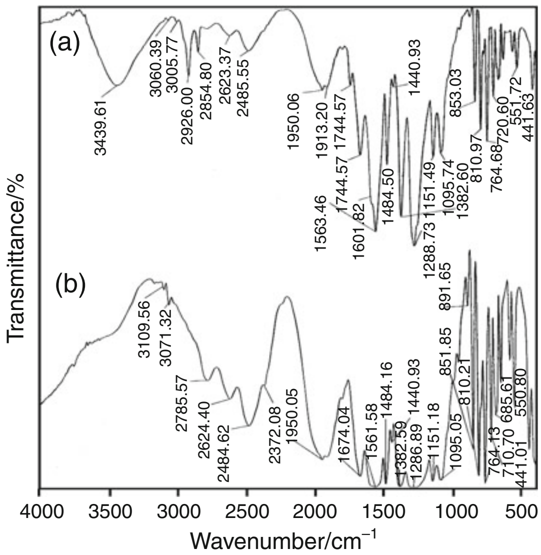

Fig. 3 FTIR spectra of (*a*) pure and (*b*) 0.012 mol dm^{-3} anthracene doped KHP crystals

Thermal studies

The simultaneous TG-DTA analysis of crystals grown from pure and anthracene added KHP solutions were carried out between 50 and 1,100 °C in nitrogen atmosphere. The investigation shows that there is no physically adsorbed water in molecular structure of crystals grown from both the solutions. Studies reveal the purity of material. TG curve shows a gradual mass loss and residual mass obtained at 1,200 °C is 17.5%. The sharpness of the peak shows the good degree of crystallinity of the material. The TG curve indicates that the sample is stable up to 300 °C. No decomposition up to the melting point (Fig. 4) ensures the suitability of material for application in lasers where the crystals are required to withstand high temperatures.

SEM

SEM study gives information about the surface nature and its suitability for device fabrication. Also it is used to check the presence of imperfections. It has been reported that effectiveness of different impurities in changing the surface morphology is different. At low concentrations of dopant, the effects are reflected by changes in configuration of grown structures. The SEM images are given in Fig. 5a and b. The SEM images of KHP show deep crack developments on the surface. A perfect layered structure is shown in SEM image (Fig. 5b) for crystal grown from anthracene doped solution. It appears that the crystalline perfection improves much better in the presence of dopant and doping results in the reduction of size of the particles.

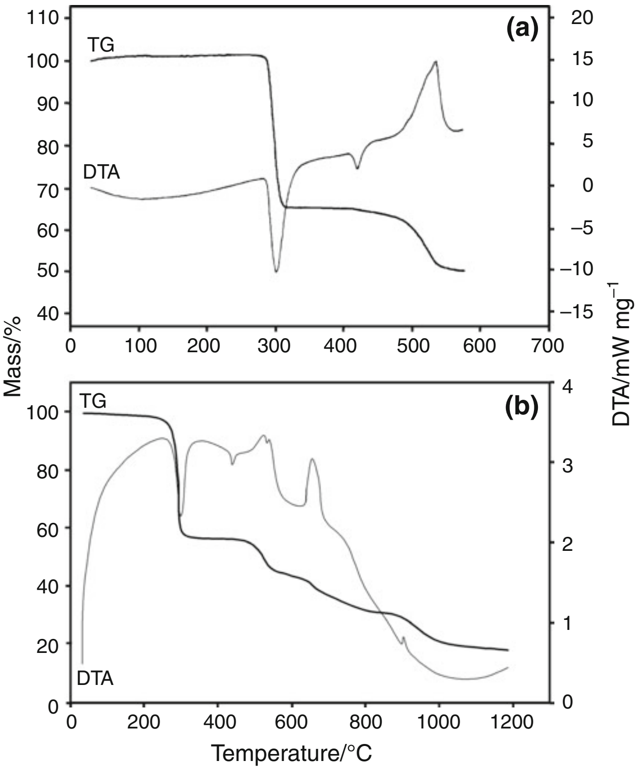

Fig. 4 TG-DTA curves of **a** pure and **b** 0.012 mol dm^{-3} anthracene doped KHP crystals

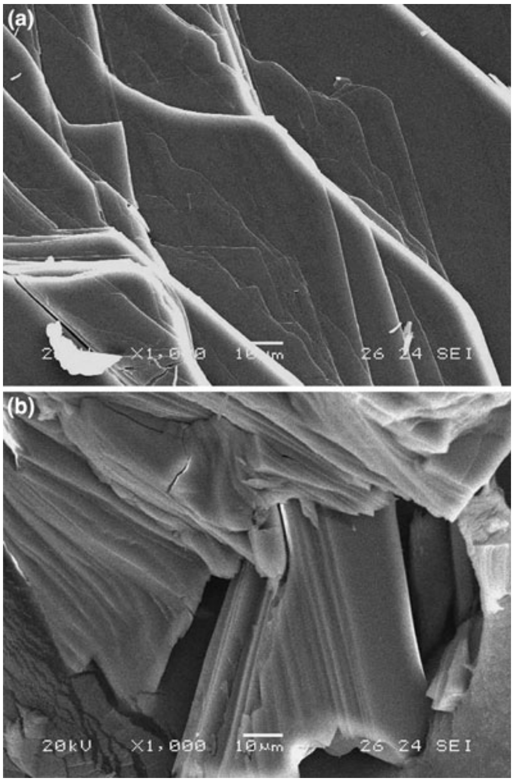

Fig. 5 SEM images of **a** pure and **b** 0.012 mol dm^{-3} anthracene doped KHP crystals

Table 1 SHG output

System	$I_{2\omega}$/mV
Pure KHP	27–29
KHP/anthracene doped	83–85

Table 2 Fluorescence intensity of anthracene doped KHP crystals

Concentration of anthracene/mol dm^{-3}	Fluorescence intensity (I_f)	λ_{emi}/nm
0.0005	19.6	404.0
0.0015	24.2	404.0
0.005	31.4	404.0
0.012	44.8	404.0

SHG efficiency

Although many materials have been identified that have higher molecular non-linearities, the attainment of second order effects requires favourable alignment of molecule within the crystal structure. The efficient SHG demands specific molecular alignment of crystals to be achieved facilitating non-linearity in the presence of dopant. It has been reported that SHG can be greatly enhanced by altering molecular alignment through inclusion complexation [59]. Intensity of second harmonic generation gives an indication of the NLO efficiency of the material

Input radiation used was 5 mJ/pulse. It is interesting to observe that the small quantity addition of highly fluorescent anthracene triply enhances the SHG efficiency of KHP (Table 1). Most likely, doping results in asymmetric charge distribution in the crystal such that a polar orientation is maintained throughout the crystal. We have previously reported that the complexing agent EDTA dramatically enhances the SHG efficiency of ZTS crystals [60].

UV–Visible spectra

The optical transmission is not altered much in the case of anthracene doping. The lower cutoff wavelength remains almost same. High percentage of transmittance in the entire visible region is observed for all the samples.

Fluorescence intensity

The fluorescence studies of the anthracene doped KHP specimens were performed. Figure 6 represents the fluorescence spectra of anthracene and various concentrations

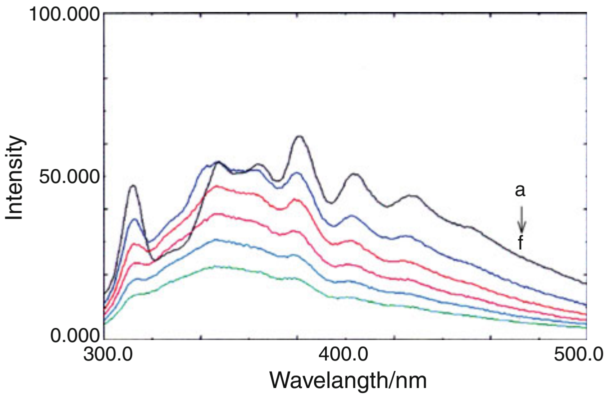

Fig. 6 Fluorescnece spectra of (*a*) pure anthracene and (*b*) 0.012 mol dm^{-3}, (*c*) 0.005 mol dm^{-3}, (*d*) 0.0015 mol dm^{-3} and (*e*) 0.0005 mol dm^{-3} anthracene doped KHP crystals

of anthracene doped KHP crystals. It is observed that increasing the anthracene concentration increases the fluorescence intensity gradually (Table 2). Although the shift in emission maximum is not appreciable, a possible bimolecular complex formation of KHP with anthracene is not ruled out. No change in λ_{max} indicates that the complex is mainly characteristic of anthracene. Concentration quenching effect as noticed in the study of naphthalene doped by anthracene [24] is not observed in the present investigations. Fluorescence spectra of anthracene doped with various concentrations of KHP reveal that KHP decreases the fluorescence intensity of anthracene and the amount of decrease depends on KHP crystals.

Conclusions

Anthracene doping did not affect the basic physical properties of the KHP crystals but improved the intensity of fluorescence emission and NLO properties. SEM studies reveal KHP suffering from crack development. XRD and FTIR spectral analyses suggest the slight distortion of the structure of crystal due to doping. UV–Visible study shows that the transparency has not been affected significantly by the dopant. It is interesting to observe that additions of small quantity anthracene to KHP results in the enhancement of fluorescence intensity. Interestingly, second harmonic generation (SHG) efficiency of KHP is dramatically improved by doping with small quantities of anthracene. Thermal analysis confirms no decomposition of the crystal up to the melting point.

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