DOI:10.7598/cst2015.1119
ISSN:2278-3458

Chemical Science Transactions
2015, **4(4),** 1095-1101

RESEARCH ARTICLE

X-Ray, Thermal and Mechanical Studies of Potassium Acid Phthalate Single Crystals Added with Aspartic Acid/*L*-Citrulline

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Received 12 August 2015 / Accepted 12 September 2015

Abstract: Potassium acid phthalate (KAP) is an interesting semi-organic optical material. Optically transparent good quality single crystals of pure and amino acid added KAP single crystals were grown by conventional slow evaporation technique at 32 ^{o}C and characterized to study the thermal and mechanical stability of the crystal. The x-ray diffraction analysis confirms the presence of amino acid molecules in the KAP crystal matrix in the case of amino acid added KAP single crystals. The thermogravimetric (TG/DTG) and microhardness measurements indicate that the amino acid addition significantly tunes the thermal stability and mechanical strength of the KAP crystal.

Keywords: Semi-organic optical materials, X-ray diffraction, Thermal stability, Mechanical property

Introduction

Single crystals of semi-organic optical materials have been grown and characterized with much interest in the last few decades due to their importance in industrial applications. Crystals of metal hydrogen phthalates ($C_6H_4COOHCOOM$, M representing alkali metals) are used as analyzers, monochromators and modulators in soft x-ray spectrometers[1]. These crystals have covalent, ionic, van der Waals and hydrogen bonds. Among these, potassium hydrogen phthalate or potassium acid phthalate (KAP) is found to be very interesting.

KAP crystallizes in the orthorhombic crystal system with space group $Pca2_1$ and KAP crystal exhibits piezoelectric, pyroelectric, ferroelectric, elastic and nonlinear optical (NLO) properties with long term stability in devices[2]. A good number of reports are available on the growth and characterization of pure and impurity added (doped) KAP single crystals[3-8]. Significant tuning of optical, thermal and mechanical properties of KAP has been observed on doping with amino acids like glycine ($C_2H_5NO_2$), *L*-alanine ($C_3H_7NO_2$), *L*-tyrosine ($C_9H_{11}NO_3$), l-lysine ($C_6H_{15}N_2O_2$), *dL*-alanine ($C_3H_7NO_2$) and *L*-methionine ($C_5H_{11}NO_2S$). Research work involving the preparation and characterization of new/modified solid state

materials in order to explore potential applications is of paramount importance both academically and industrially. Research work involving the preparation and characterization of new/modified solid state materials in order to explore potential applications is of paramount importance both academically and industrially. So, in this context it is worth investigating the influence of large molecular amino acids like aspartic acid ($C_4H_7NO_4$) and *L*-citrulline ($C_6H_{13}N_3O_3$) as additives on the physical properties of KAP.

In the present work, we have grown pure and large molecular amino acid (aspartic acid/*L*-citrulline) added KAP single crystals by the slow evaporation method and characterized structurally, thermally and mechanically by x-ray diffraction (XRD), thermogravimetric (TG/DTG) and microhardness measurements. The results obtained are reported herein and discussed.

Experimental

Commercially available analytical reagent (AR) grade chemicals were used for the experimental work. Millipore water with the resistivity of 18.2 MΩcm at 25 ^oC was used as the solvent. Pure and amino acid (aspartic acid/*L*-citrulline) added KAP single crystals were grown at room temperature (32 ^oC, controlled to an accuracy of ±0.01 ^oC) by the slow evaporation method. Saturated aqueous solutions were prepared in beakers by adding the amino acid in KAP solution as required and stirred well using a magnetic stirrer. Thus prepared solutions were filtered using a micro filter paper and kept in a constant temperature bath. The beakers were covered with perforated sheets and the solutions were allowed to equilibrate. Three different amino acid concentrations *viz*. 0.01, 0.05 and 0.1 M was considered in each case. So a total of seven crystals were grown. Single crystals with good transparency were harvested within a span of 25 days. Photographs of the sample crystals grown are shown in Figure 1. Hereafter, the grown crystals can be represented as: KAP (pure KAP), LA (0.01 M aspartic acid added KAP), MA (0.05 M aspartic acid added KAP), HA (0.1 M aspartic acid added KAP), LC (0.01 M *L*-citrulline added KAP), MC (0.05 M *L*-citrulline added KAP), HC (0.1 M *L*-citrulline added KAP).

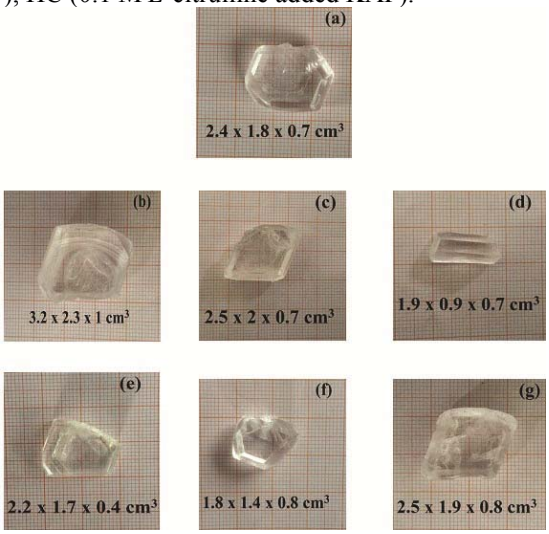


Figure 1. Photographs of the grown crystals: (a) KAP, (b) LA, (c) MA, (d) HA, (e) LC, (f) MC and (g) HC

Results and Discussion

XRD measurements were carried out on powdered samples of all the seven grown crystals using a Bruker AXS D8 Advance diffractometer equipped with a 2θ compensating slit with monochromatized CuK_α radiation of wavelength 1.54 Å. The data were collected in a continuous scan mode with a step size of 0.02˚ and step time of 1 sec over a of 2θ range of 10 to 50˚. The XRD patterns observed in the present study are shown in Figure 2. The sharp peaks observed confirm the crystalline nature of the grown crystals. The patterns observed are in good agreement with that reported in the literature for the pure KAP crystal[9]. This indicates that the material of the grown crystals is basically KAP. The small changes in 2θ values due to doping indicate that the dopant molecules have entered into the KAP crystal matrix. The reflection peaks were indexed and the lattice parameters were determined using the standard procedures. The obtained lattice parameters are provided in Table 1. The non-observance of significant changes in the lattice parameters due to doping implies that the crystal structure is not distorted significantly.

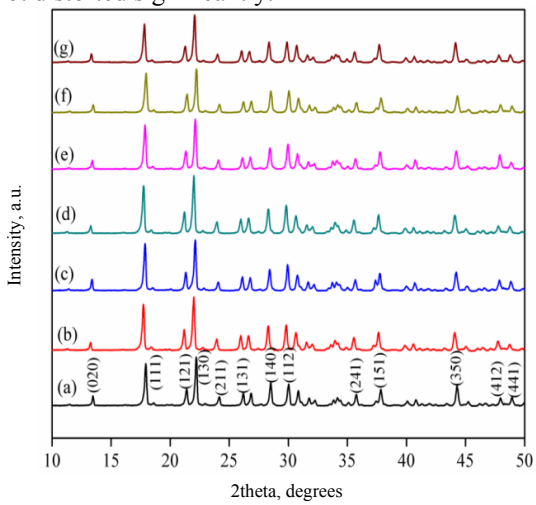


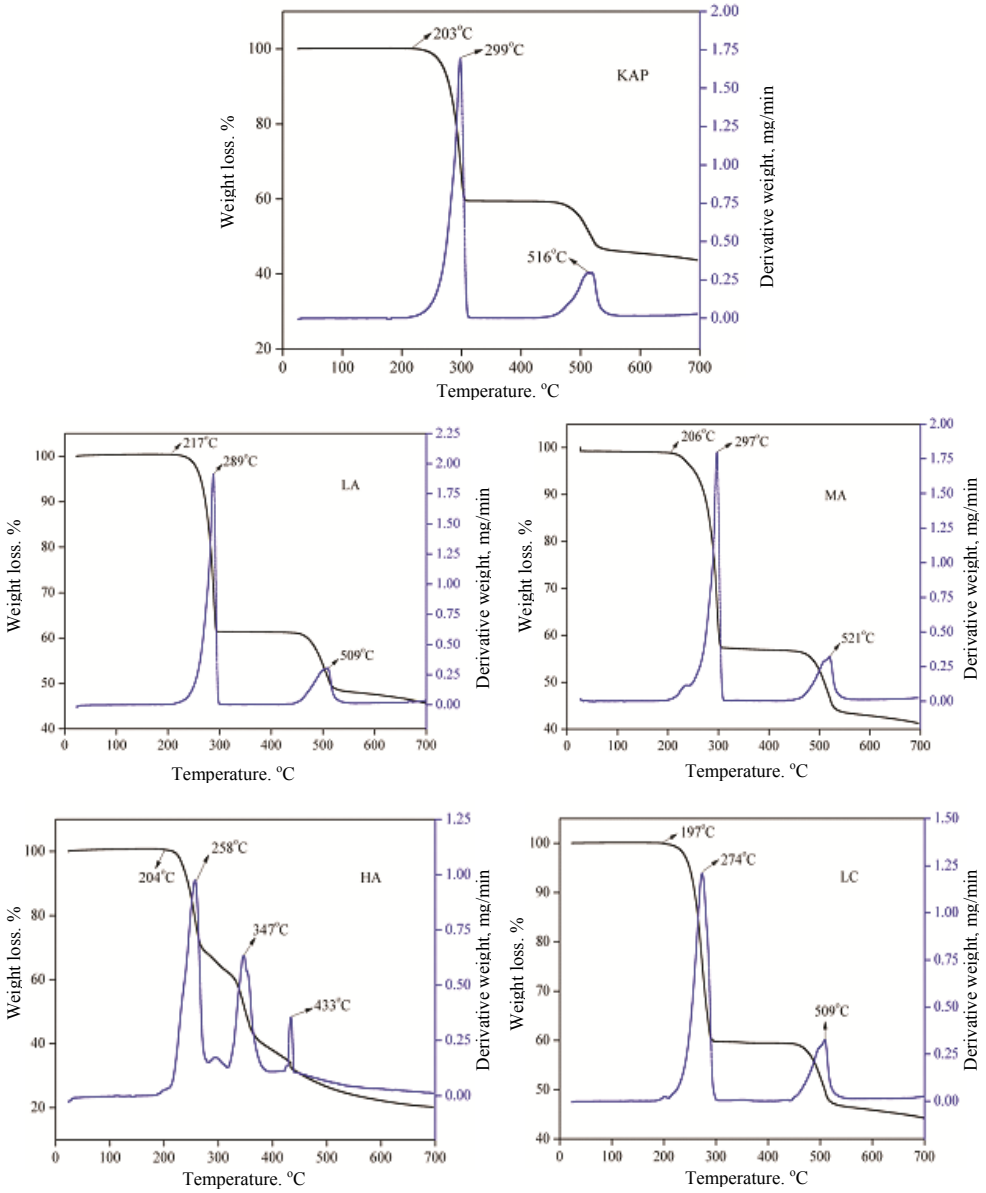
Figure 2. XRD patterns for the grown crystals: (a) KAP, (b) LA, (c) MA, (d) HA, (e) LC, (f) MC and (g) HC.

Table 1. Lattice parameters for the grown KAP crystals

Crystal	a (Å)	b (Å)	c (Å)	V (Å^3)
KAP	9.592	13.248	6.442	818.7
LA	9.631	13.338	6.492	834.0
MA	9.603	13.280	6.481	826.6
HA	9.628	13.342	6.485	833.1
LC	9.603	13.284	6.455	823.6
MC	9.614	13.314	6.477	829.2
HC	9.619	13.310	6.475	829.1

Thermogravimetric analysis (TG/DTG) was carried out for all the seven crystals grown using a TGA Q500 V6.7 Build 203 instrument with pin-holed platinum crucibles heated at 10 ˚C/min under nitrogen atmosphere. The thermal stability of the grown crystals was determined by carrying out thermogravimetric (TG/DTG) measurements. The thermograms obtained in the present study are shown in Figure 3. The TG curve obtained for the pure KAP

is in good agreement with that reported in the literature[10,11]. The weight loss data are provided in Table 2. Results indicate that LA exhibits maximum thermal stability (up to 217 ^{o}C) and LC exhibits minimum thermal stability (up to 197 ^{o}C). Further, non-observance of weight loss within 100 ^{o}C indicates the absence of adsorbed water molecules in the crystal during crystallization. All the crystals except HA exhibit two sharp weight losses. HA exhibits three weight losses; the first two are sharp and the third one is diffuse. This indicates some small distortion created in the crystal due to higher concentrated aspartic acid at higher temperature, after the first decomposition (formation of dipotassium phthalate).



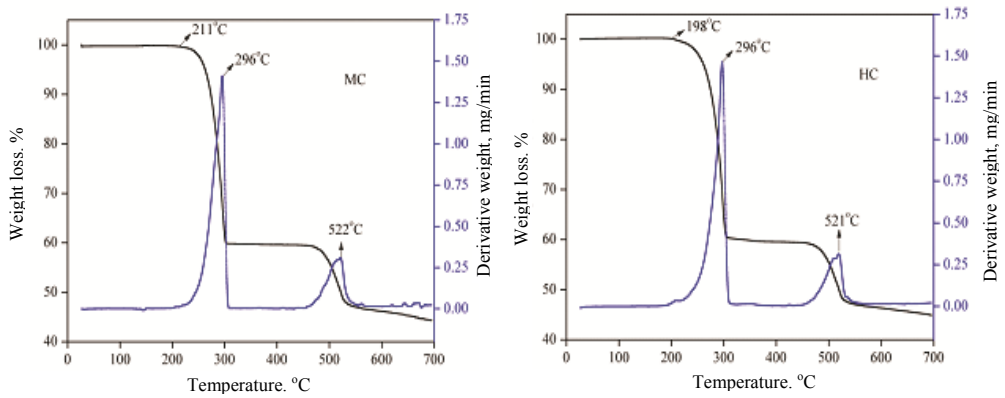


Figure 3. TG/DTG patterns observed for the grown crystals.

Table 2. Decomposition temperatures and percentage weight losses for the grown crystals.

Crystal	First decomposition temperature, °C	Weight loss, %	Rate of weight loss mg/min At, °C	Second decomposition temperature, °C	Weight loss, %	Rate of weight loss, mg/min at, °C
KAP	203-303	41	1.69 at 299	458-537	12	0.30 at 516
LA	217-293	39	0.59 at 289	454-528	13	0.29 at 509
MA	206-306	43	1.80 at 297	459-550	13	0.32 at 521
HA	204-268	31	0.97 at 258	228-366	28	0.63 at 347
LC	197-292	41	1.21 at 274	448-532	11	0.32 at 509
MC	211-305	41	1.41 at 296	464-538	12	0.30 at 522
HC	198-305	40	1.46 at 296	461-543	13	0.31 at 521

Within the temperature range considered in the present study (30-700 °C), the thermal decomposition of KAP takes place in two stages. In the first stage, dipotassium phthalate is formed with the removal of phthalic anhydride and water from two molecules of KAP. In the second stage, potassium carbonate contaminated with elementary carbon is formed with the evolution of acetaldehyde. The reaction in the two stages can be represented as

$$2KC_8H_5O_4 \xrightarrow[\text{Stage I}]{-(C_8H_4O_3 + H_2O)} K_2C_8H_4O_4 \xrightarrow[\text{Stage II}]{-(C_2H_4O)} K_2CO_3 + \text{Carbon}$$

Microhardness measurements were carried out on {010} face of the crystal using a Vickers microhardness tester (Shimadzu HMV-2T) fitted with diamond indenter for three different loads, *viz*. 25, 50 and 100 g. It is a fact that any material useful for optical devices must satisfy at least a minimum requirement of atmospheric, thermal and mechanical stabilities. In order to understand the mechanical stability of the grown crystals, microhardness measurements have been carried out by using the Vickers indentation method with a constant indentation time of 5 seconds for all loads considered. The Vickers microhardness number was calculated using the relation

$$H_v = 1.8544P/d^2 \text{ (kg/mm}^2\text{)}$$

Where, P is the applied load and d is the diagonal length of the impression. Load *versus* H_v plots obtained are shown in Figure 4. Results indicate that the hardness value increases with the increase in load for all the seven crystals grown in the present study. Also, the lower

concentrated doping increases while the middle and higher concentrated doping decreases the hardness value. The changes in the hardness value due the addition of amino acid may be due to the interaction between O-H group of KAP with COO group of amino acid. Higher the hardness values greater is the stress required to form dislocation, thus confirming greater crystalline perfection especially for the lower concentrated aspartic acid/*L*-citrulline doped crystals[12]. The well known Meyers relation is stated as

$$P=K_1d^n$$

Where, K_1 is the standard hardness value (material constant) and n is the work hardening coefficient (Meyers index number). The n value can be determined by fitting the hardness data into Meyers relation. Plots between log P and log d (shown in Figure 5) are found to be nearly linear and the n value has been determined from the slope of the best fitted straight lines. According to Onitsch, the value of n should lie between 1 to 1.6 for hard materials and greater than 1.6 for soft materials. In the present study, all the seven grown belongs to the soft material.

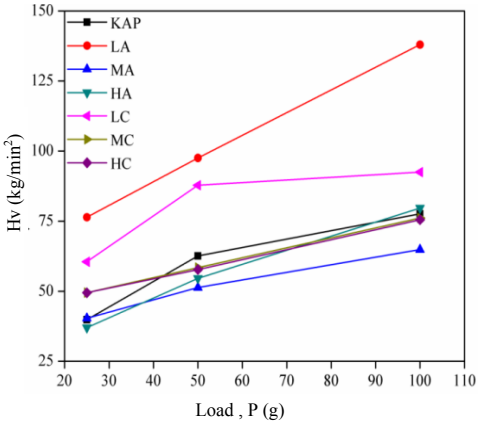


Figure 4. Vickers hardness plots for amino acid added KAP crystals

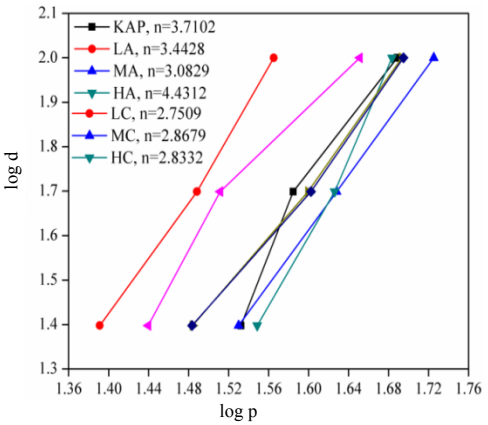


Figure 5. Plots between log P and log d for amino acid added KAP crystals

Conclusion

Good quality, atmospherically stable, colourless and transparent single crystals with reasonably good size of pure and aspartic acid/L-citrulline added KAP have been successfully grown by the slow evaporation method at 32 °C. The XRD analysis confirms the basic material of all the seven crystals grown as KAP and also the incorporation of amino acid molecules into the KAP crystal matrix in the case of doped crystals. All the grown crystals are found to be thermally and mechanically stable so that they can very well be utilized in possible devices.

Acknowledgement

The authors (C Amuthambigai) acknowledge PSN management for providing the research stipend to carry out the work in a great manner. The authors are happy to thank Dr. S. Natarajan, Framework Solids Laboratory, IISc, Bangalore, for providing powder XRD facilities and Dr. U.P. Senthil Kumar, Vice President, Orchid Pharma, Chennai for providing TGA facilities.

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