High Temperature Phases of NH_4-KH_2PO_4 (AKDP) Crystals Studied by TG-DTA Method

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Abstract

Crystals of (1:15) and (1:20) molar ratios of Ammonium Dihydrogen Phosphate, $NH_4H_2PO_4$ (ADP) and Potassium Dihydrogen Phosphate, KH_2PO_4 (KDP) (AKDP15 and AKDP20) were grown by slow evaporation method at room temperature from aqueous saturated solutions. High temperature phases of the as-grown crystals were characterized by simultaneous Thermogravimetric and Differential Thermal Analysis method to investigate the decomposition and melting temperatures of the crystals. TG-DTA thermograms were observed in the temperature range of 30°C – 600°C. TG-DTA thermograms of AKDP15 and AKDP20 were compared to that of the thermograms of undoped KDP crystal.

Keywords: KDP, AKDP, TG-DTA, High temperature phases

INTRODUCTION

Since the discovery of second harmonic generation (SHG) of ruby laser radiation in a quartz crystal by using Franken in 1961, the search for new crystals with good frequency conversion properties continues even today [2]. The very first material to be used and exploited for their non linear optical (NLO) and electro-optic (EO) properties was Potassium Dihydrogen Phosphate, KH_2PO_4 (abbreviated as KDP). With the aim of improving the SHG efficiency of KDP, research workers have attempted to modify KDP crystals by doping different types of impurities. There are only few reports available on the effect of ammonium (NH_4) salts on the NLO efficiency of KDP crystals [1, 7].

Crystal of Potassium Dihydrogen Phosphate, KH_2PO_4 belongs to the scalenohedral (twelve-sided polyhedron) class of tetragonal crystal system and has created considerable interest among several research workers [2, 7, 8]. A research programme on the growth, structural, optical and thermal characterizations of pure and impurities added KDP and ADP crystals are on hand in our laboratory. As a part of the programme, in the present work, high temperature phases of the (1:15) and (1:20) molar ratios of ADP doped KDP crystals (abbreviated as AKDP15 and AKDP20) were studied by simultaneous Thermogravimetric and Differential Thermal Analysis (TG-DTA) method. High temperature phases of decomposition and melting processes of the crystals were reported by using TG-DTA thermograms.

MATERIALS AND METHOD

Growth of AKDP15 and AKDP20 Single Crystals

Crystals can be grown in multiple ways and in multiple environments. Sometimes changing the ways that crystals are grown and the environments that they are grown in will have an effect on the crystal structure, mass, color or other attributes of the crystals. If the substance chosen is soluble in water, specimens are usually best prepared by crystallization from the appropriate solvent. Inorganic salts are usually soluble enough in water [1, 4, 6].

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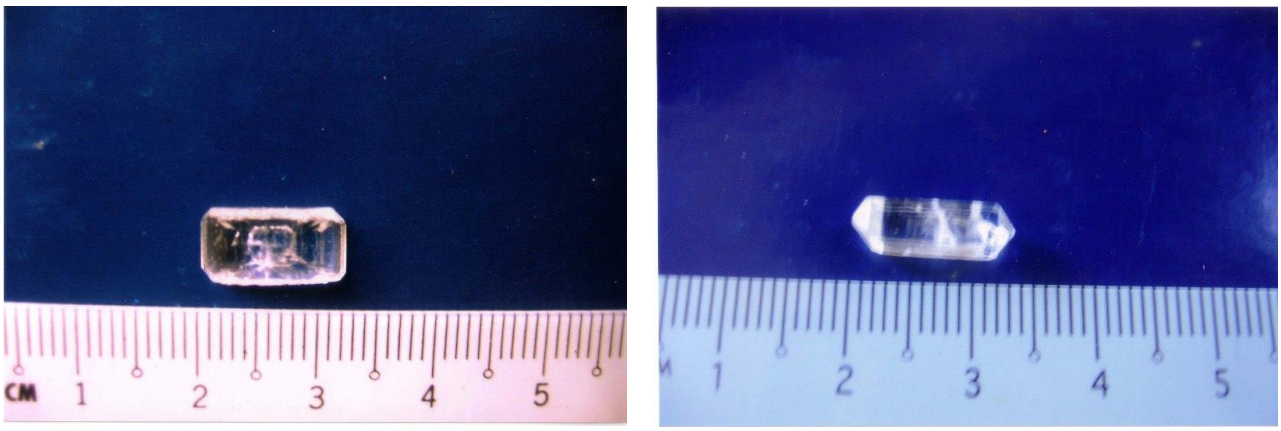
In the present study, crystals of AKDP15 and AKDP20 were grown by slow evaporation method from the aqueous saturated solutions of (1:15) and (1:20) molar ratios of Ammonium Dihydrogen Phosphate, $NH_4H_2PO_4$ (ADP) and Potassium Dihydrogen Phosphate, KH_2PO_4 (KDP). The distilled-water was used as the solvent [4, 7]. At room temperature, the crystals are colourless. Photographs showing the as-grown AKDP15 and AKDP20 crystals are shown in Fig 1(a) and (b).



(a) (b)

Figure (1). Photographs of the as-grown (a) AKDP15 and (b) AKDP20 crystals.

TG-DTA Measurement

Thermal analyses of the AKDP15, AKDP20 and KDP crystals were investigated by using (SHIMADZU) DTG-60H Thermal Analyzer which is shown in Fig 2. Aluminium (Al) pan was used as the standard sample.

Figure (2). Photograph showing the (SHIMADZU) DTG-60H Thermal Analyzer.

A complete thermal analysis of the sample yields the information concerning chemical composition and structure of the material. TG-DTA method can be used to investigate the phase transition, dehydration, decomposition, crystallization, mass variation and melting of

the samples. TG-DTA thermograms of AKDP15, AKDP20 and KDP crystals are shown in Fig 3 to 5. As shown in DTA thermogram of AKDP15 crystal, the two endothermic reaction peaks of step-wise characteristics are found at 239°C and 267°C. These two peaks are indicated by the dehydration of water (H_2O) and decomposition of ammonium (NH_4) from the sample occurred while TG thermogram shows the mass variation of 12.57%. In DTA thermogram, small endothermic reaction peaked at 317°C is represented by the melting of the sample.

Also, as shown in DTA thermogram of AKDP20 crystal, the two endothermic reaction peaks of step-wise characteristics are found at 243°C and 270°C respectively. These two peaks are indicated by the dehydration of water (H_2O) and decomposition of ammonium (NH_4) from the sample occurred while TG thermogram shows the mass variation of 14.06%. In DTA thermogram, small endothermic reaction peak at 322°C is represented by the melting of the sample.

In thermogram of undoped KDP crystal (see Fig 5), one endothermic reaction peak is found at 203°C in DTA thermogram that indicates the dehydration of water during the crystal growth condition. After reaching the temperature at 310°C, the sample is found to be melted. TG thermogram shows the mass variation of sample with 12.20% due to water dehydration.

From the TG-DTA thermograms, the dehydration and melting temperatures of the undoped KDP is found to be the lowest one. Comparison of the dehydration temperatures and melting temperatures of the KDP, AKDP15 and AKDP 20 crystals are shown in Figure (6.a. and b).

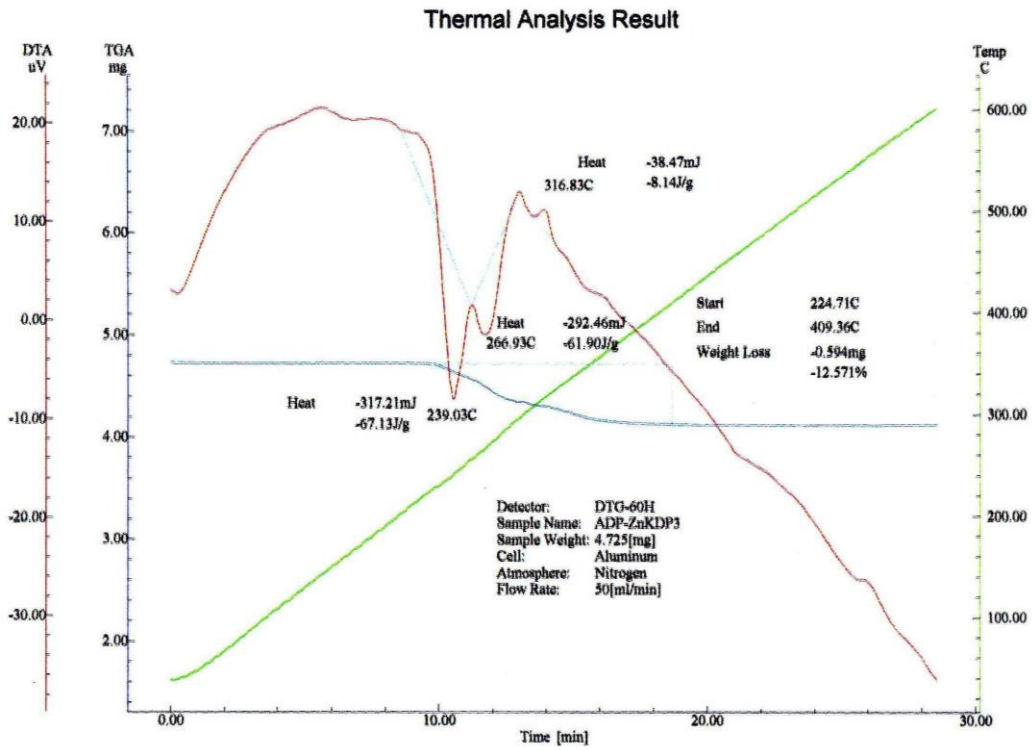


Figure (3). TG-DTA thermograms of AkDP15 crystal.

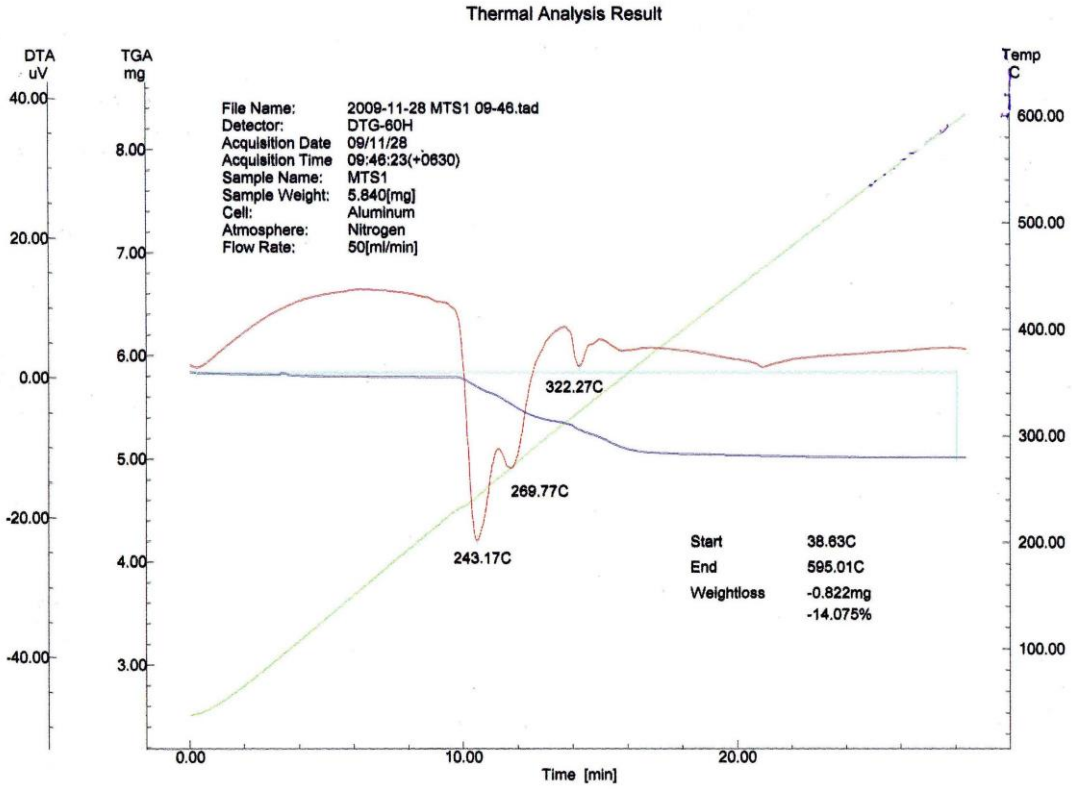


Figure (4). TG-DTA thermograms of AKDP20 crystal.

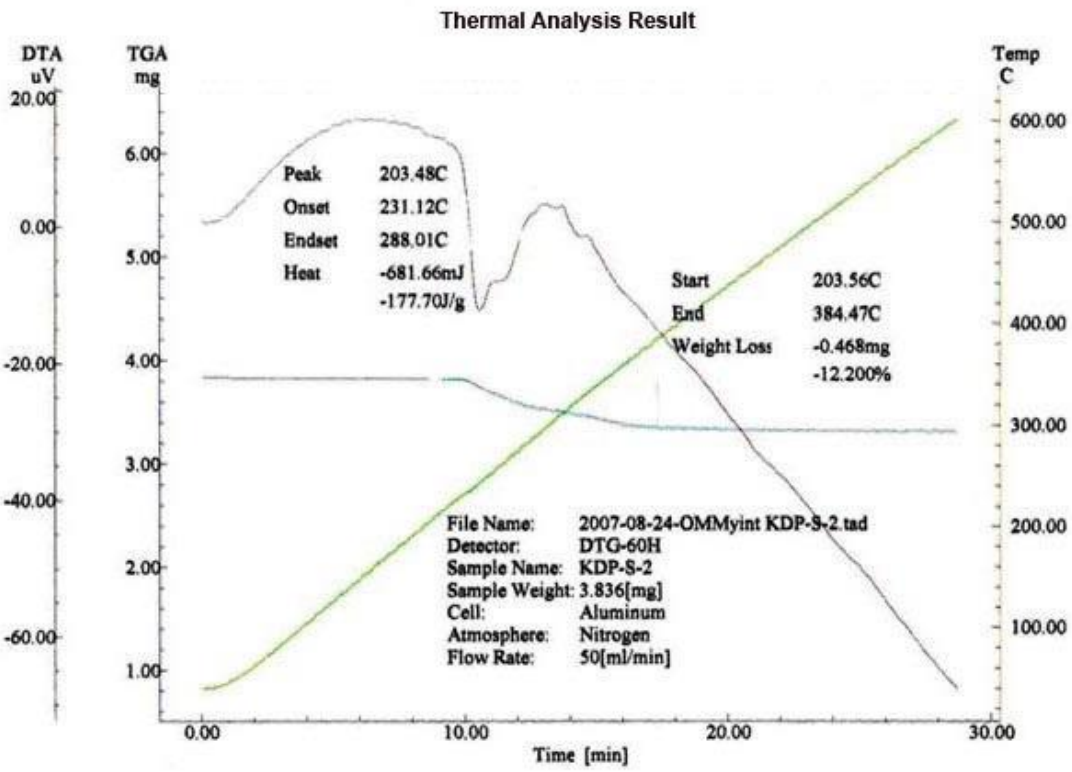
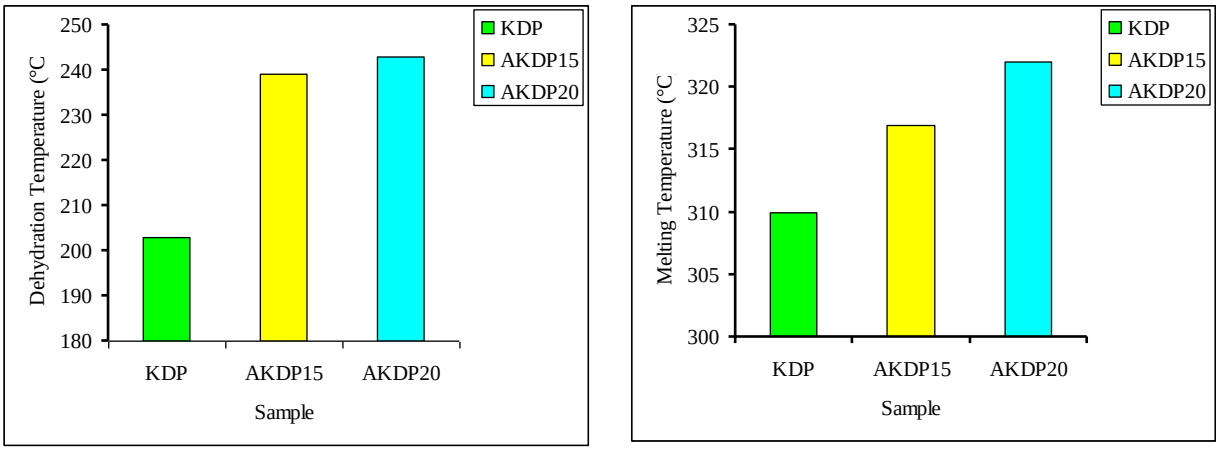


Figure (5). TG-DTA thermograms of KDP crystal.



(a) (b)

Figure (6). Comparison of the (a) dehydration temperatures and (b) melting temperatures of the KDP, AKDP15 and AKDP 20 crystals.

CONCLUSION

Crystals of (1:15) and (1:20) molar ratios of Ammonium Dihydrogen Phosphate, $NH_4H_2PO_4$ (ADP) and Potassium Dihydrogen Phosphate, KH_2PO_4 (KDP) (AKDP15 and AKDP20) were grown and characterized by TG-DTA method. From the TG-DTA thermograms, the dehydration temperatures of the crystals are obtained as 239°C for AKDP15, 243°C for AKDP20 and 203°C for undoped KDP respectively. The melting points of the crystals are also found to be 317°C for AKDP15, 322°C for AKDP20 and 310°C for undoped KDP. It can be seen that the dehydration and melting temperatures of the undoped KDP are found to be the lowest one.

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