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THERMAL STABILITY OF CsH_2PO_4

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ABSTRACT

The thermal behaviour of CsH_2PO_4 (CDP) was investigated using micro TG, DSC, X-ray and optical microscopy. The loss in weight commences at 508 K and levels off at 688 K. Although there is no water of hydration as such in this compound, the overall loss in weight corresponds to one molecule of H_2O, giving $CsPO_3$. Concomitant with this "dehydration", CDP also undergoes a reversible polymorphic phase transition at 508 K, as evidenced by DSC and optical microscopic data. The process of "dehydration" might go through an intermediate, $Cs_2H_2P_2O_7$, as in the case of NaH_2PO_4.

INTRODUCTION

CsH_2PO_4(CDP) is the latest ferroelectric material of the series of dihydrogen phosphates with general formula MH_2PO_4, where M = alkali metal. While all the other members of this family have a tetragonal unit cell, CsH_2PO_4 has a monoclinic one [1]. The high temperature behaviour of CDP has been studied recently by Metcalfe and Clark [2] using DSC between *RT* and 520 K. There was an ambiguity in the ΔH values in their work. Further, the thermal stability of the compound in this temperature range was not examined. We investigated the thermal behaviour of CDP up to 700 K using different techniques.

EXPERIMENTAL

An appropriate amount of Cs_2CO_3 was dissolved in H_3PO_4 and the pH was adjusted to about 2.5. The solution was allowed to crystallise by slow evaporation at room temperature. Single crystal tablets of about 5 mm × 5 mm × 3 mm were obtained. For all experimental observations, except microscopic ones, powdered samples of the optically good crystals were used. The identity of the material was established using X-ray powder technique.

An indigenously fabricated micro TG set-up [3] with a sample size of ~10 mg and a sensitivity of ±1 μg was used. A Perkin-Elmer DSC-1 B, and a

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crimped sample size ~15 mg and a heating/cooling rate of 8°C min^{-1} were employed. A Leitz Ortholux-2-Pol BK polarising microscope with a Leitz 350 hot stage was used.

RESULTS

The micro TG run of CDP with a heating rate of 4°C min^{-1} from *RT* to 700 K is shown in Fig. 1. The loss in weight starts from 508 K and levels off at 688 K and corresponds to 7.1% of the initial CDP weight. This corresponds very closely to the removal of one molecule of water from CDP leaving a residue of $CsPO_3$. A fresh sample of CDP was heated on the micro TG from *RT* up to 508 K and held there for 30 min, followed by heating at the same rate of 4°C min^{-1} up to 680 K. The loss in weight at the end of the isothermal treatment of 30 min at 508 K was about one half of what was observed after complete dehydration.

Figure 2 shows a typical DSC scan of CDP during the first heating. The sample was thermally cycled several times and our observations can be summarised as follows.

(a) During the first heating a transition at 508 K with $\Delta H = 8.4 \pm 0.8$ kJ $mole^{-1}$ was observed.

(b) If the heating was terminated at 515 K and cooled back to *RT*, a multiplet of transitions was obtained in the temperature range 480--460 K [Fig. 2 (b)].

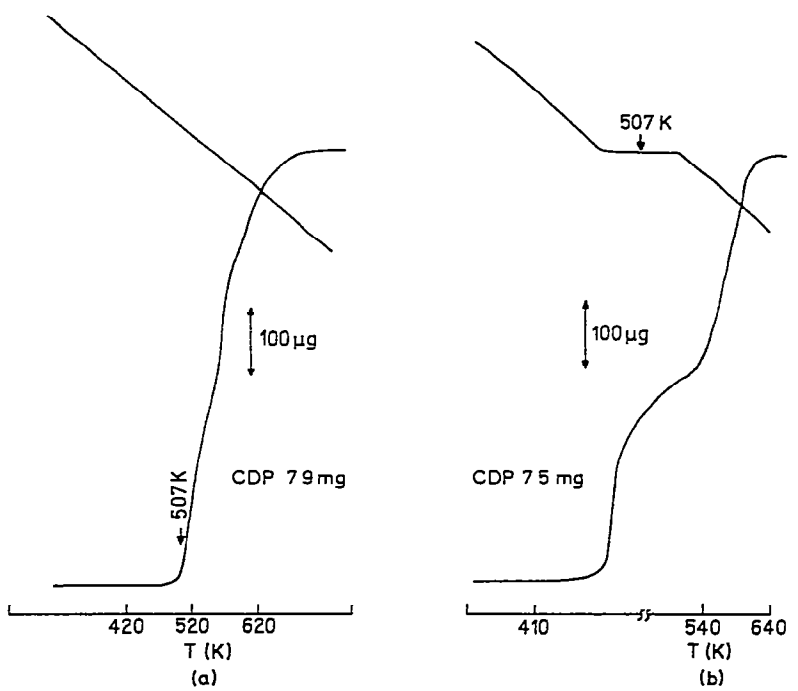

Fig. 1. Micro TG runs of CDP (a) from *RT* to 700 K at 4°C min^{-1} and (b) from *RT* to 508 K at 4°C min^{-1}, kept there for 30 min and then heated to 700 K at 4°C min^{-1}.

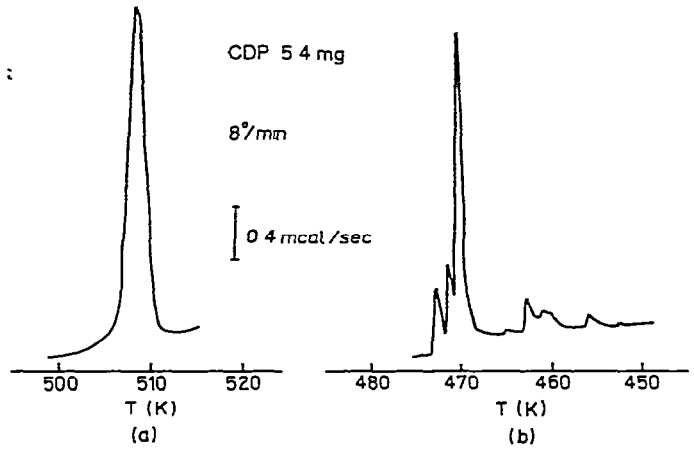

Fig. 2. DSC scans of CDP. (a) heating and (b) cooling cycles.

(c) In subsequent heating cycles, the 508 K peak was obtained with progressively lower ΔH values, while the cooling cycle gave the multiplet with diminishing intensity.

(d) If during a heating cycle the run was terminated at 480 K, i.e. without traversing the 508 K peak, and cooled back to RT, the multiplet was absent.

(e) If during the first heating cycle heating was continued beyond 520 K, a broad endotherm (characteristic of decomposition) with ΔH = 13.4 ± 2 kJ mole^{-1} was obtained with a peak at 547 K.

(f) Cooling from 590 K to RT and subsequent heating did not show any transition.

The X-ray powder pattern of CDP at RT is shown in Table 1. The pattern at 515 K was different from that at RT. The pattern at 575 K did not show any sharp diffraction lines due to the non-crystalline nature of the product.

A tiny single crystal of CDP was viewed on the hot stage of the microscope under crossed-polars (at 45° position) while being heated at about 4°C min^{-1}. The crystal, which was colourless at the start, remained so up to 505 K and remained a single crystal as was judged by rotation on the microscopic stage. Around 505 K the crystal showed brilliant "Pol" colours which changed quickly, turning dark around 510 K. Above this temperature the crystal, which fragmented, was not optically isotropic. However, the birefringence is small.

DISCUSSION

From the micro TG data two things become clear. First, the loss in weight commences at 508 K and ends at 688 K. Second, the total loss in weight in this temperature interval corresponds to one molecule of water per CDP unit at the start of the reaction, leaving a residue of $CsPO_3$.

In DSC the endothermic peak at 508 K is due to a transformation of CDP to a high temperature form. From the micro TG it is clear that at 508 K the

TABLE 1

X-ray powder pattern of CDP at RT (Z = 2, monoclinic unit cell)

Sample No.	d values		Relative Intensity	hkl
	Obsd.	Calcd.	I/I_0	
1	4.843	4.863	W	$1\bar{1}0$
2	4.623	4.627	W	$\bar{1}01$
3	3.739	3.745	100	$\bar{1}11$
4	3 181	3 188	W	020
5	3.058	3.060	40	$\bar{2}11$
6	2.933	2.935	W	120
7	2.629	2.626	W	021
8	2.430	2.431	20	220
9	2.368	2.373	20	$\bar{3}11$
10	2.314	2.314	20	$\bar{2}02$
11	2.178	2.177	W	012
12	2.042	2.041	W	$\bar{3}02$
13	1.993	1.994	W	$\bar{3}21$
14	1.929	1 931	W	$\bar{1}31$
15	1.873	1.874	W	022
16	1.746	1.748	W	202
17	1.634	1.634	W	$\bar{3}31$
18	1.612	1.612	W	$\bar{2}03$
19	1.595	1.594	W	040
20	1.500	1.501	W	013
21	1.467	1.467	W	$\bar{2}40$
22	1.443	1.442	W	$\bar{4}31$
23	1.393	1.394	W	113
24	1.349	1.349	W	322
25	1.313	1.313	W	$0\bar{4}2$
26	1.288	1.288	W	$\bar{6}11$
27	1 267	1.267	W	$\bar{5}13$
28	1.249	1.249	W	033
29	1.228	1.228	W	$5\bar{3}0$
30	1.216	1.216	W	$\bar{6}21$
31	1 201	1.201	W	$\bar{3}04$

W = Intensity less than 10%

Least squares fit gave the following lattice constants.

$a_0 = 7.899 \pm 0.059$ Å, $b_0 = 6.376 \pm 0.048$ Å, $c_0 = 4.866 \pm 0.037$ Å,

$\alpha = 90°$;

$\beta = 107.82° \pm 0.01$;

$\gamma = 90°$

loss in weight just commences and hence this strong peak in DSC is not due to decomposition. The fact that, while heating, a single strong transition is observed in DSC, while during cooling, a multiplet of peaks is observed with a large temperature hysteresis, suggests that the transition is reversible and involves several steps. During the heating cycle, due to the possibility of superheating, the different steps might not have been resolved. However, while cooling, varying hysteresis behaviour of different steps make the resolution possible. This is very similar to what was observed in the case of

Na_2SO_4 [4]. The progressive reduction in the ΔH values of the 508 K peak during successive thermal cycles between RT and 515 K can be explained by a slow but finite dehydration taking place at 515 K, the point of termination of each heating cycle. This is corroborated by the micro TG data. Metcalfe and Clark [2] quoted two different ΔH values of 1.07 and 7.62 kJ $mole^{-1}$ for the 508 K transition of CDP in different contexts in their paper. They did not mention the thermal history of the transition that gave their ΔH value. Our value of 8.4 kJ $mole^{-1}$ is closer to that of 7.62 kJ $mole^{-1}$.

Since the sample was crimped, the product of decomposition, H_2O, cannot easily escape. This raises the temperature of dehydration slightly, thereby allowing a clear separation of the phase transition and dehydration peaks.

The X-ray pattern of CDP at RT can be indexed in terms of its known [1] monoclinic unit cell, as shown in Table 1. From the isothermal TG treatment mentioned above it is clear that about 50% of the material is dehydrated at 508 K, even after keeping the sample for 30 min. Thus the X-ray pattern at 515 K should be that of a mixture of equal amounts of the high temperature form of CDP and the product of dehydration, $CsPO_3$. However, the X-ray pattern of completely dehydrated CDP at 700 K did not show any diffraction lines due to its non-crystalline nature. This is consistent with the known polymeric nature [5] of $CsPO_3$. The X-ray pattern at 515 K is therefore assumed to be that of the high temperature form of CDP.

The optical microscopic observation of quickly changing "Pol" colours around 510 K can be directly attributed to a phase change wherein anomalous variations in thermal expansion and refractive index contribute to such effects as have been reported [6] in the case of $NaBF_4$.

In the case of NaH_2PO_4 it was reported [5] that dehydration takes place in two steps at two distinctly different temperatures.

$$2\,NaH_2PO_4 \xrightarrow[\Delta]{442K} Na_2H_2P_2O_7 + H_2O$$

$$Na_2H_2P_2O_7 \xrightarrow[\Delta]{513K} (NaPO_3)_x + H_2O$$

Parallel to this, our data on micro TG may be explained as

$$2\,CsH_2PO_4 \xrightarrow{T=508K} Cs_2H_2P_2O_7 + H_2O$$

$$Cs_2H_2P_2O_7 \xrightarrow[T>508K]{} (CsPO_3)_x + H_2O$$

This is consistent with the micro TG data mentioned above including the isothermal one. However, a DSC scan of CDP held at 515 K for 60 min and cooled back to RT showed the presence of CDP at RT. This is contrary to the formation of $CsH_2P_2O_7$ as intermediate at 508 K.

It might be added here that in CDP there are two linear networks of the H atom, one ordered and the other disordered. There are no such groups of atoms of H and O to be considered as water molecules in the unit cell. However, the loss in weight corresponds to the loss of two atoms of H and one atom of O per CDP unit. Hence, dehydration may not be an appropriate term. Disproportionation could be a more apt term in this case.

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