Thermochimica Acta, 24 (1978) 149–153

DIFFERENTIAL SCANNING CALORIMETRY OF RbH_2PO_4 AND CsH_2PO_4

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(Received 28 June 1977)

ABSTRACT

The high-temperature phase behaviour of RbH_2PO_4 and CsH_2PO_4 have been studied. RbH_2PO_4 undergoes a single quasi-irreversible phase transition with an enthalpy of 4.665 kJ mol^{-1}. The transition is found to occur over the temperature range 86–111 °C. CsH_2PO_4 undergoes two transitions at 149 and 230 °C. The lower one is quasi-irreversible and has an enthalpy of 4.284 kJ mol^{-1}. The one at 230 °C is reversible and has an enthalpy of 1.071 kJ mol^{-1}.

INTRODUCTION

RbH_2PO_4(RDP) and CsH_2PO_4(CDP) are KH_2PO_4(KDP)-type hydrogen-bonded ferroelectrics[1]. The main interest in these compounds is derived from their low-temperature ferroelectric transition. The present study is aimed at the temperature region above ~ 20 °C.

The high-temperature phase relations of KDP serve as a model for the group and therefore merit discussion. The ferroelectric phase is orthorhombic space group C_{2v}^{19}-Fdd2 and this transforms on heating to the paraelectric tetragonal phase, space group D_{2d}^{12}-I$\bar{4}$2d. This transition occurs at −151 °C with an entropy[1] of 4.05(0) J K^{-1} mol^{-1}. At higher temperatures, KDP decomposes and this factor considerably complicates the interpretation of the phase relations. High pressures inhibit this decomposition and therefore high-pressure differential thermal analysis studies[2] have been vital to a clearer understanding of the phase relations. At ~ 180 °C a quasi-irreversible transition to a monoclinic phase with uncertain space group[1–3] occurs, and this phase then transforms at ~ 233 °C to a totally uncharacterized phase of KDP which finally melts at 260 °C. The use of the word quasi-irreversible refers to the *a* transition that occurs on heating but the reverse transition does not occur on cooling to room temperature. This allows the high-temperature phase to be retained metastably for a period of days. After a certain period, the substance does revert to the stable phase.

RDP is ferroelectric in its orthorhombic phase, space group C_{2v}^{19}-Fdd2, and it transforms at −126 °C to its paraelectric phase which is tetragonal space group D_{2d}^{12}-I$\bar{4}$2d. At high temperatures, the problem is how many transitions exist and

where decomposition begins. A quasi-irreversible transition at ~ 86°C to a monoclinic phase[4, 5] has been reported with decomposition occurring between 125 and 200°C[4, 6–10]. Certain authors have observed two transitions at ~ 90°C and ~ 110°C[6, 10]. D'yakov *et al.*[10] have reported enthalpies of transition as 1500 and 50 cal mol^{-1}. The present work on RDP will attempt to resolve the question of whether one or two transitions occur.

CDP differs slightly from the other members of the series in that the paraelectric phase is monoclinic, space group C_{2h}^2-$P2_1/m$[11]. No high-temperature studies have been reported.

EXPERIMENTAL

A commercial differential scanning calorimeter (DuPont 990 Thermal Analyser) was used in all DSC measurements. All measurements were made in aluminium cups with Al_2O_3 as a reference and the heating rate used was 2°C min^{-1}. The sensitivity of the calorimeter was varied over the range 0.05 to 10 mcal s^{-1}. The temperature of transition was determined by measuring the point of intersection of the line extrapolated through the straight-line portion of the DSC curve leading edge and the baseline. The peak area was determined by measuring the area enclosed by the peak and the line drawn from the point where the DSC curve departs from the baseline to the point where it returns. All temperature and enthalpy measurements were calibrated with respect to an indium standard (m.p. 156.6°C). The loss of weight by samples was monitored to an accuracy of 0.05 mg.

The RDP studied was obtained in the form of single crystal chips[12]. The CDP was prepared by neutralizing solutions of Merck Cs_2CO_3 (purity 99.5%) with H_3PO_4 using methyl orange as an indicator. The solid was precipitated by adding alcohol. The precipitate was filtered, vacuum-dried and baked at 80°C for ~ 12 h. Both the RDP and CDP were well characterized using Guinier X-ray powder diffraction techniques.

RESULTS AND DISCUSSION

RbH_2PO_4

The present results on RDP seem to present sufficient evidence to conclude that only one transition exists in the range 80–120°C. The quasi-irreversible nature of the transition was confirmed. The main problem encountered was that the transition temperature was found to vary from one sample to the next. As the samples were all in the form of single crystal chips (~ 10 × 10 × 1 mm) and came from the same source, no fundamental difference existed between chips. Three sizes of samples were used which established a definite pattern. When chips having edge lengths of ~ 4 × 2 mm (thickness ~ 1 mm) were used, one transition was found at 86°C. Those with edge lengths of ~ 2 × 1 mm (thickness ~ 1 mm) yielded one transition at ~ 103–111°C. Finely powdered samples showed a transition that started at ~ 99°C and decomposi-

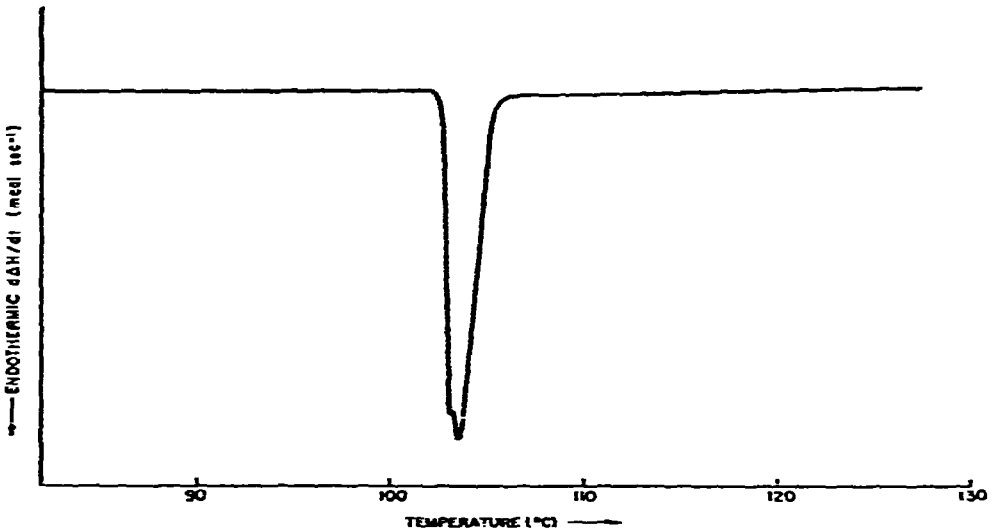

Fig. 1. DSC curve of RbH_2PO_4.

tion took place while this transition was still in the process of occurring. Figure 1 shows a typical DSC trace of a small solid sample, with a calorimeter sensitivity of 2 mcal s^{-1}. No weight loss was encountered in the solid samples to ~ 130°C. Enthalpy measurements carried out at calorimeter sensitivities of 1, 2 and 10 mcal s^{-1} $in.^{-1}$ were respectively 4.665, 5.100 and 5.824 kJ mol^{-1}.

The present results support the workers claiming only a single transition, but the influence of factors such as sample size on the DSC measurements could explain the large spread in the reported transition temperature. The present work shows no evidence of a second transition. The work of D'Yakov et al.[10] reports the enthalpies of the transitions as 1.500 and 0.05 kcal mol^{-1}. Although the enthalpy of the first transition corresponds to that found in the present work, it is difficult to understand how they were able to report a value of 0.05 kcal mol^{-1} for the second transition from their data. The fact that they mention that the second transition was obscured on occasions by the first transition suggests a spread in the transition temperature.

CsH_2PO_4

Two endothermic transitions occurred on heating CDP; the lower temperature transition occurred at 149°C and was quasi-irreversible whereas the higher temperature transition took place at 230°C and was reversible. Figure 2 shows a DSC trace of the first transition using a calorimeter sensitivity of 0.5 mcal s^{-1}. The enthalpy of this transition was found to be 1.071 kJ mol^{-1}. Figure 3 shows a DSC trace of the second transition using a calorimeter sensitivity of 5 mcal s^{-1}. The enthalpy of this transition was found to be 7.615 kJ mol^{-1}. Weight-loss measurements were made on specimens which had been taken through each transition. It was found that after passing through the first transition, specimens had suffered no loss in weight. However, after passing through the second transition the weight loss was ~ 1.5%.

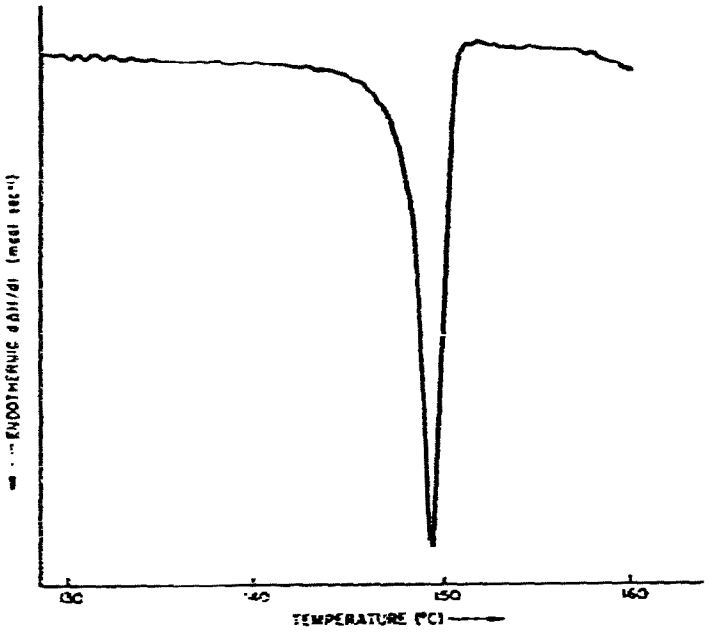

Fig. 2. DSC curve of transition at 149°C in CsH_2PO_4.

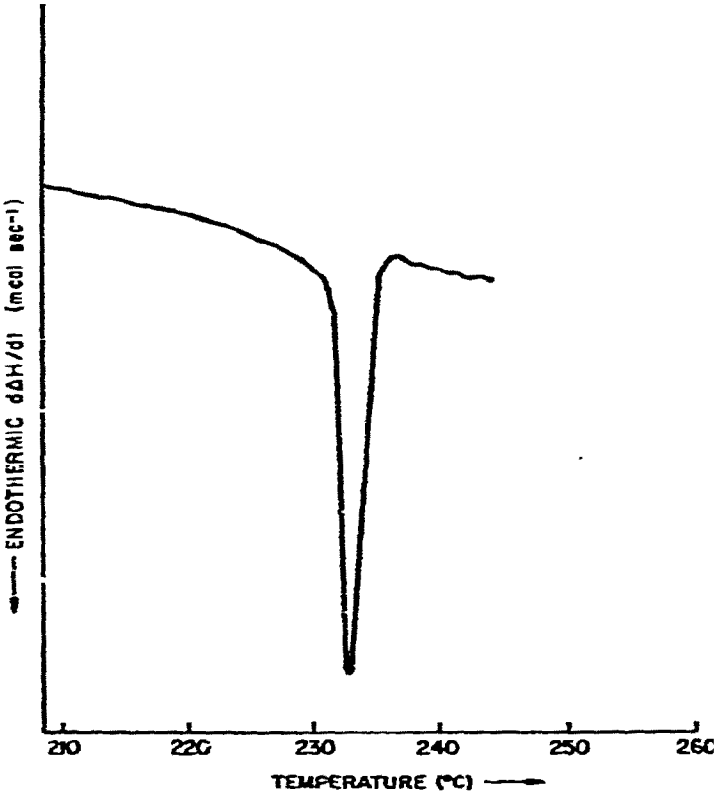

Fig. 3. DSC curve of transition at 230°C in CsH_2PO_4.

The quasi-irreversible transition at 149°C is similar in nature to the quasi-irreversible transitions found for KDP and RDP. This would lead us to postulate that the present transition is the counterpart of the transition found for KDP and RDP. The structural data[11] on CDP show that this is not the case as CDP is monoclinic prior to the transition while KDP and RDP are tetragonal.

The transition at 230°C is certainly a real phase transition and not a decomposition process. The weight loss of ~ 1.5% is substantially less than the 10–30% weight losses encountered in the decomposition processes characteristic of the KDP-family. Most of the studies of the decomposition of members of the KDP-family show an initial weight loss of ~ 1% at ~ 50°C prior to the major loss in weight. The background obtained in Fig. 3 shows that this is indeed the case and that a typical catastrophic decomposition process can be expected to occur at slightly higher temperatures.

CONCLUSION

(1) RDP shows a single quasi-irreversible transition where a large spread in transition temperature is encountered. The transition occurs between 86 and 111°C. No evidence is found that a second phase transition exists prior to the expected decomposition process.

(2) The enthalpy of this transition is 4.665 kJ mol^{-1}.

(3) CDP shows two phase transitions at 149 and 230°C prior to decomposition at > 250°C. The transition at 149°C is quasi-irreversible.

(4) The enthalpies of these transitions are 1.071 and 7.615 kJ mol^{-1}, respectively.

REFERENCES

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