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THERMAL DECOMPOSITION OF MAGNESIUM ACETATE TETRAHYDRATE UNDER SELF-GENERATED ATMOSPHERE

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ABSTRACT

The dehydration of magnesium acetate tetrahydrate was studied by simultaneous TG–DTG–DTA under various sealed atmospheres (open, quasi-sealed, and completely sealed). It had been reported for this salt that dehydration was a single-stage loss of water. In the case of quasi-sealed systems (29.8, 60 and 100 $\mu m\phi$ tungsten wires), however, stable monohydrate was obtained

$$Mg(CH_3COO)_2 \cdot 4\,H_2O \rightarrow Mg(CH_3COO)_2 \cdot H_2O + 3\,H_2O$$

$$Mg(CH_3COO)_2 \cdot H_2O \rightarrow Mg(CH_3COO)_2 + H_2O$$

Monohydrate is easily removed from the apparatus, and identified by means of X-ray diffraction.

INTRODUCTION

In the case of the thermal decomposition of producing gases, the equilibrium will be attained for the partial pressure of the gases and the decomposition will be influenced by the composition of the atmosphere. Q-derivatography (quasi-isothermal and -isobaric thermogravimetry), which applies well to self-generated atomospheres, has been devised and good results obtained. The thermal decomposition of ammonium heptamolybdate (6-)tetrahydrate, $(NH_4)_6Mo_7O_{24} \cdot 4\,H_2O$ (AHM), was studied by means of simultaneous TG–DTG–DTA [1]. It was found that H_2O and NH_3 were produced at the same time under both static air atmosphere and flow conditions of various gases. This system also used Q-derivatography and home-built quasi-sealed thermogravimetry. It was proposed that the reaction can be separated into two steps. However, as a result of studies of reproducibility and sample size, it was concluded that the sample size should be made as small as possible. Micro-Q-TG will be needed in order to study the dehydration reaction.

A quasi-sealed system was applied to about a 10-mg sample and good results were obtained in the case of calcium sulfate dihydrate ($CaSO_4 \cdot 2$

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H_2O) [2] and magnesium sulfate heptahydrate ($MgSO_4 \cdot 7\ H_2O$) [3]. In the case of $CaSO_4 \cdot 2\ H_2O$ [2], the dehydration reaction was a single-stage loss of water under an open system, however, under completely and quasi-sealed systems the reaction could be separated into two stages. The hemihydrate analysis was carried out with this apparatus. In the case of $MgSO_4 \cdot 7\ H_2O$ [3], only the monohydrate ($MgSO_4 \cdot H_2O$) intermediate was confirmed under a completely sealed system, whereas the tri-, di-, and monohydrates ($MgSO_4 \cdot 3\ H_2O$, $MgSO_4 \cdot 2\ H_2O$, and $MgSO_4 \cdot H_2O$, respectively) were confirmed under a quasi-sealed system.

In this communication, the dehydration of magnesium acetate tetrahydrate, $Mg(CH_3COO)_2 \cdot 4\ H_2O$, is studied by means of simultaneous TG–DTG–DTA under various atmospheres, corresponding to three systems (open, completely sealed, and quasi-sealed). Moreover, new intermediate compounds of the reaction stage are confirmed by means of high-temperature oscillation X-ray diffraction with a rotating anode-type large capacity generator.

The synthesis of magnesium acetate monohydrate from solution has already been reported [4]. The thermal decomposition of magnesium acetate tetrahydrate has also been reported [5,6].

The analysis of magnesium acetate monohydrate was carried out under a quasi-sealed system without solution and was confirmed as monohydrate by the percent weight-loss of TG and high-temperature X-ray analysis.

EXPERIMENTAL

Materials

Magnesium acetate tetrahydrate (Kanto Co.) was used in powder form. The sample sizes used were generally 10.0 mg and the reference material used for DTA was α-Al_2O_3.

Apparatus

A modified thermoflex 8002 (Rigaku Denki Co.) was used for simultaneous TG–DTG–DTA measurement. The range of temperature covered was usually from room temperature to 420°C and the sample was heated in most cases at a rate of $1°C\ min^{-1}$. The range of TG used was usually 10 mg and the range of DTA used was $\pm 100\ \mu V$ (upper limit corresponds to the exothermic reaction).

A JEOL-ROTEX rotating anode-type large capacity generator (model JRX-12) was used for the high-temperature and high-temperature oscillation X-ray diffraction. The temperature of the hot stage was controlled by an ULVAC-RIKO thermal program controller (model HPC-5000 series).

Sealing techniques

The techniques of completely sealed and quasi-sealed systems had already been described [2]. In the case of a completely sealed cell, the critical explosion pressure was thought' to be above 3 atm [7], however, by the present examination it was redetermined to be above 7.3 atm.

RESULTS AND DISCUSSION

Open system

With a platinum cell (Fig. 1), simultaneous TG–DTG–DTA measurements were taken. The magnesium acetate tetrahydrate samples were 10.0 mg. A typical result is shown in Fig. 2.

On the TG curve, the loss of water starts at 56°C and finishes at 136°C. The product at 136°C was recognized as anhydrous magnesium acetate from

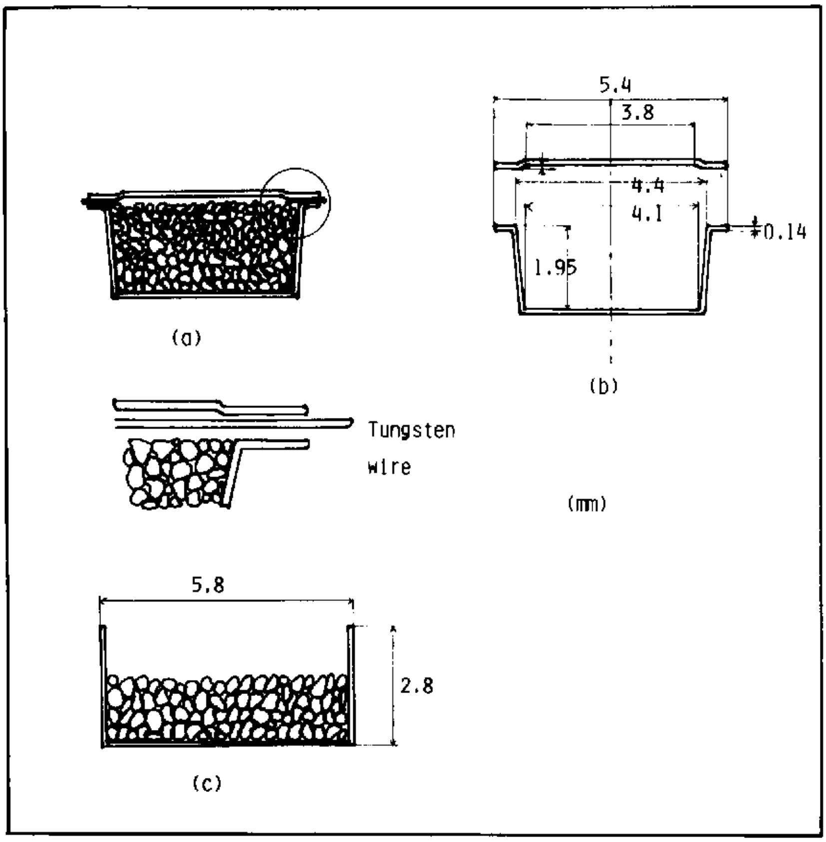

Fig. 1. (a) Schematic diagram of sample cell, aluminium cell. (b) Dimensions of sample cell. (c) Schematic diagram of sample cell, platinum cell.

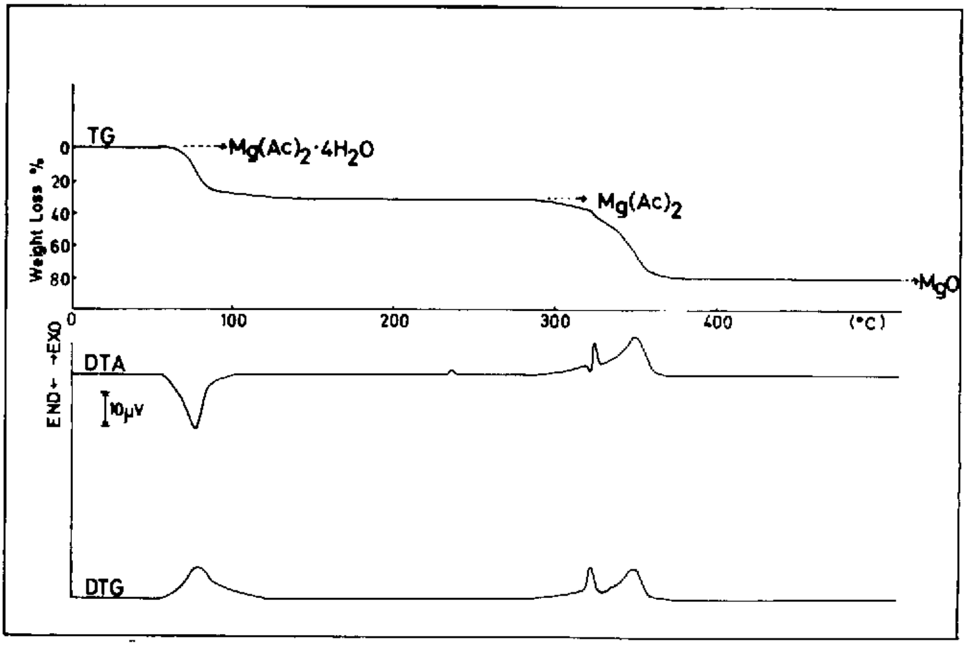

Fig. 2. TG–DTG–DTA of magnesium acetate tetrahydrate under an open system. Sample-mass, 10.03 mg; cell, platinum; heating rate, 1°C $\min^{-1}$.

a calculation of weight-losses. On the DTA curve, the endothermic peak owing to dehydration is shown at 77°C. Since no intermediate stages are shown on the TG curve, and only one peak is shown on the DTG and DTA

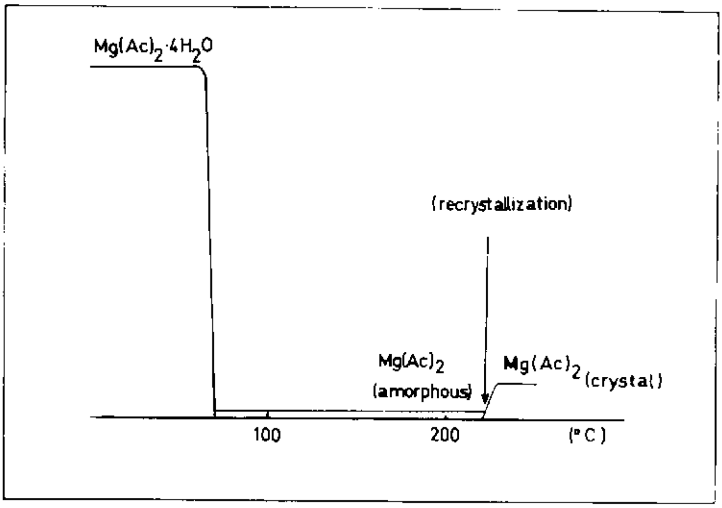

Fig. 3. High-temperature oscillating X-ray diffraction pattern of magnesium acetate tetrahydrate. Heating rate, 2°C $\min^{-1}$; range of oscillation angle, $9.49° < 2\theta < 15.29°$; oscillation speed, 8° $\min^{-1}$; X-ray source, Cu K_α, 80 mA and 40 kV; counting rate, 2×10^4 cps; time constant, 0.2 s.

curves, for the open system, the dehydration reaction is thought to be a single-stage loss of water.

After producing anhydrate, the sample is thermally stable until 286°C on the TG curve, but on the DTA curve a weak exothermic peak appears at 235°C. This exothermic process was attributed to recrystallization from the amorphous state [5,6], since there are no mass-changes corresponding to this process and there is a marked change in the high temperature oscillation X-ray diffraction pattern (Fig. 3).

For the high temperature oscillation X-ray diffraction pattern, the intensity of magnesium acetate tetrahydrate decreases rapidly at 68°C (Fig. 3). This reaction-end temperature is 68°C lower than that of the TG measurement. This is thought to be due to the sample dissolving in the dissociated water of the crystal, and the crystal structure of magnesium acetate tetrahydrate breaking. Furthermore, the intensity of the anhydrous magnesium acetate after recrystallization increases above 230°C.

The thermal decomposition of magnesium acetate anhydrate begins at 288°C and ends 375°C on the TG curve. The product was recognized as magnesium oxide from a calculation of weight-loss. On the DTA curve, as soon as decomposition starts, the exothermic process is quite clear from the endothermic peak at 322°C, a sharp exothermic peak at 326°C, and a broad exothermic peak having a peak-top at 350°C. However, the mechanism of thermal decomposition could not be solved.

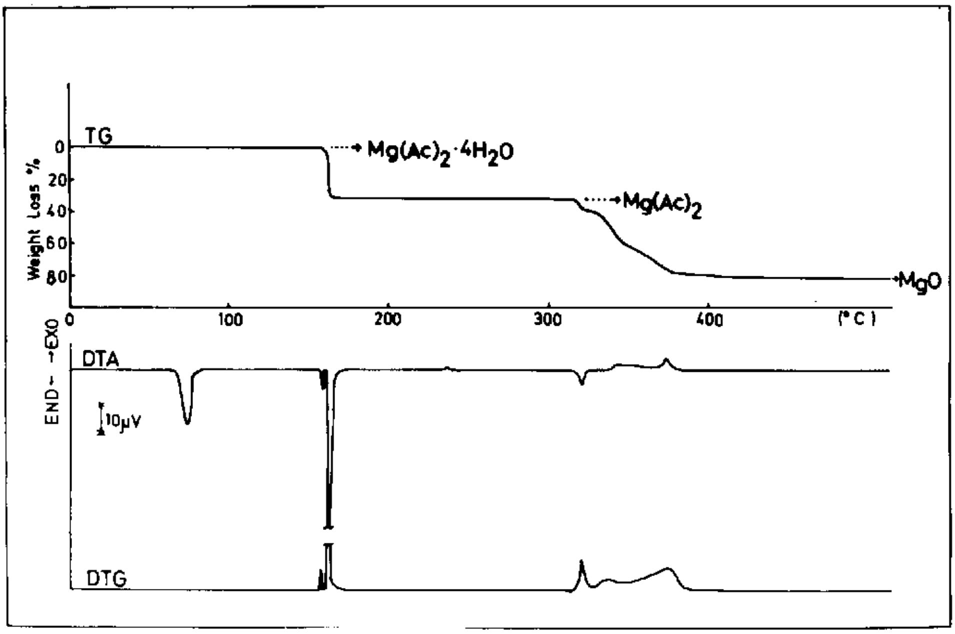

Fig. 4. TG–DTG–DTA of magnesium acetate tetrahydrate under a completely sealed system. Sample-mass, 10.00 mg; cell, aluminium; heating rate, 1°C min^{-1}.

Completely sealed system

Putting the sample into an aluminium cell, and sealing completely, simultaneous TG–DTG–DTA measurements were taken. Other conditions were, however, similar to those of the open system. The results for a 10.00-mg sample of magnesium acetate tetrahydrate are shown in Fig. 4.

On the TG curve, a sudden explosive loss of water is shown at 159°C, similar to the experimental systems of decomposition of calcium sulfate dihydrate [2] and magnesium sulfate heptahydrate [3]. The percent weight-loss of this dehydration is consistent with that of the change from magnesium acetate tetrahydrate to an anhydrate (33.6%). The product was thought to be magnesium acetate anhydrate. For the results of DTA, before explosion, an endothermic peak appears at 76°C. An endothermic peak associated with the explosion appears at 159°C. The endothermic process at 76°C is thought to be caused by the dissociation of water of crystal and the dissolution of the sample into dissociated water of crystal. After heating to 80°C, the sample cell was removed from the apparatus and opened at room temperature. The sample was in a glassy state, as shown in Fig. 5. Therefore, the very weak exothermic process was attributed to the change of crystal structure.

The thermal decomposition of magnesium acetate anhydrate started at 317°C and ended at 420°C.

Quasi-sealed system

By placing thin tungsten wire (29.8, 60, 100, 130, 150 and 200 $\mu m\phi$) between an aluminium pan and cover, measurements of the quasi-sealed system were taken. In each case the results of TG are shown in Fig. 6. The

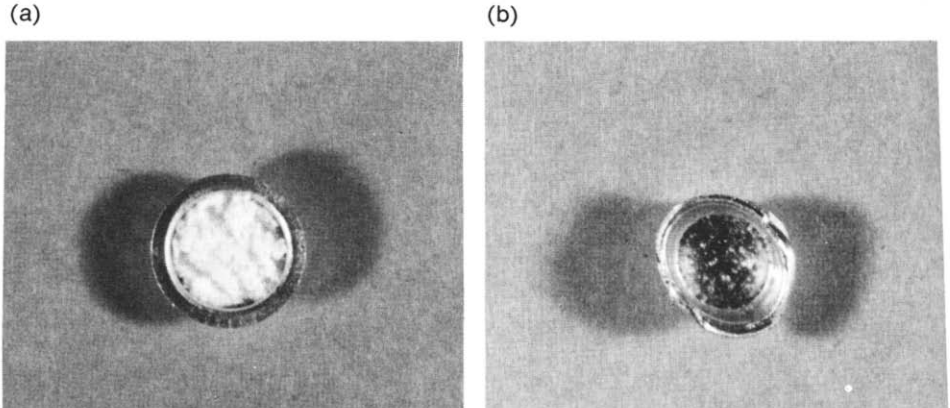

Fig. 5. (a) Represents the sample of magnesium acetate tetrahydrate; (b) represents the sample removed from the thermobalance at a temperature of 80°C under a completely sealed system.

typical TG–DTG–DTA results for interposing 60 $\mu m\phi$ tungsten wire are shown in Fig. 7.

On the TG curve, the decrease due to dehydration starts at 89°C, and is steepest from 116 to 130°C. From 140 to 170°C no changes on the TG curve are observed. After that temperature the gradual loss of water starts, ending at 195°C. From a calculation of weight-losses, the products at 140 and 195°C seem to be magnesium acetate monohydrate and magnesium acetate anhydrate, respectively. According to the above results, a dehydration of magnesium acetate tetrahydrate may be considered as follows

$$Mg(CH_3COO)_2 \cdot 4\ H_2O \rightarrow Mg(CH_3COO)_2 \cdot H_2O + 3\ H_2O$$

$$Mg(CH_3COO)_2 \cdot H_2O \rightarrow Mg(CH_3COO)_2 + H_2O$$

On the DTA curve, the endothermic peaks were recognized at 69, 73, 121, and 186°C, and the exothermic peak appeared at 238°C. The endothermic process at 69°C is thought to correspond to the dissociation of water of crystal

$$Mg(CH_3COO)_2 \cdot 4\ H_2O(s) \rightarrow Mg(CH_3COO)_2(s) + 4\ H_2O(l)$$

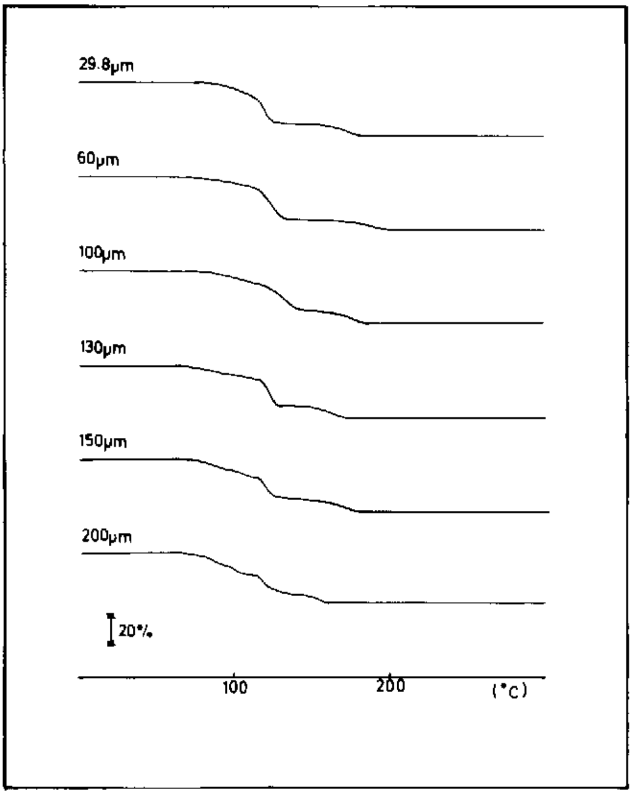

Fig. 6. TG results of magnesium acetate tetrahydrate under a quasi-sealed system.

The next endothermic process at 73°C is thought to be caused by the dissolution of water of sample into the dissociated water of crystal [8]. The endothermic process at 121°C is thought to be caused by the evaporation of three molecules of water

$$Mg(CH_3COO)_2(aq) \rightarrow Mg(CH_3COO)_2 \cdot H_2O(s) + 3\ H_2O(g)$$

The fourth endothermic process corresponds to dissociation of a molecule of water as described below

$$Mg(CH_3COO)_2 \cdot H_2O(s) \rightarrow Mg(CH_3COO)_2(s) + H_2O(g)$$

The exothermic process is thought to be attributed to crystallization from the amorphous state

$$Mg(CH_3COO)_2(\text{amorphous}) \rightarrow Mg(CH_3COO)_2(\text{crystal})$$

After heating to 150°C, the cell was removed from the apparatus, and the sample was transferred to a new cell. Tungsten wire (60 $\mu m\phi$) was placed between the aluminium pan and cover, measurements of the quasi-sealed system were taken. The results are shown in Fig. 8. The weight-loss started at 155°C and ended at 187°C. The percent weight-loss corresponded to that of the change from magnesium acetate monohydrate to an anhydrate (11.23%). The X-ray diffraction pattern of the former sample was consistent with the

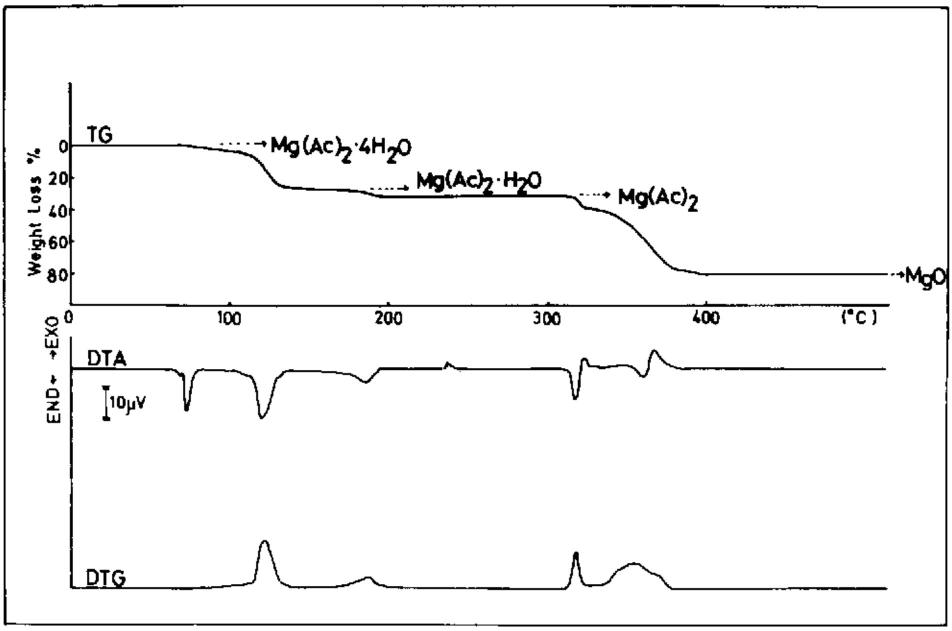

Fig. 7. TG–DTG–DTA of magnesium acetate tetrahydrate under a quasi-sealed system (using 60 $\mu m\phi$ tungsten). Sample-mass, 10.01 mg; cell, aluminium; heating rate, 1°C min^{-1}.

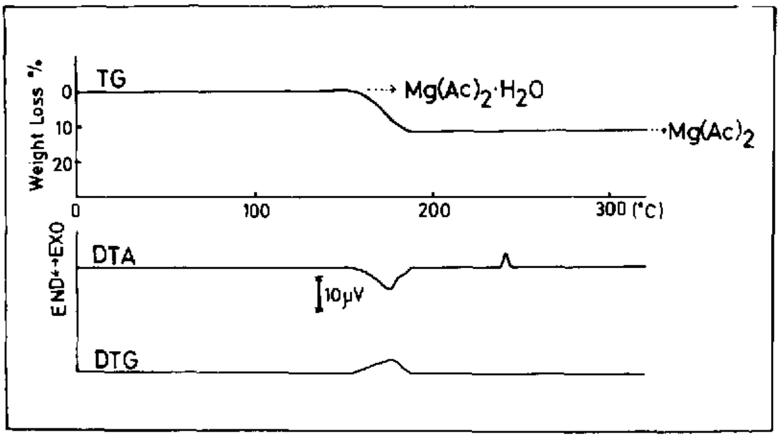

Fig. 8. TG–DTG–DTA of magnesium acetate monohydrate under a quasi-sealed system (using 60 μmϕ tungsten). Sample-mass, 8.85 mg; cell, aluminium; heating rate, 1°C min^{-1}.

ASTM card of magnesium acetate monohydrate [9]. Furthermore, from the high-temperature oscillation X-ray diffraction, the peak intensity of magnesium acetate monohydrate diffraction decreases rapidly at 151°C (Fig. 9). As mentioned above, it was recognized that magnesium acetate monohydrate could be removed from the apparatus, and identified by means of X-ray diffraction.

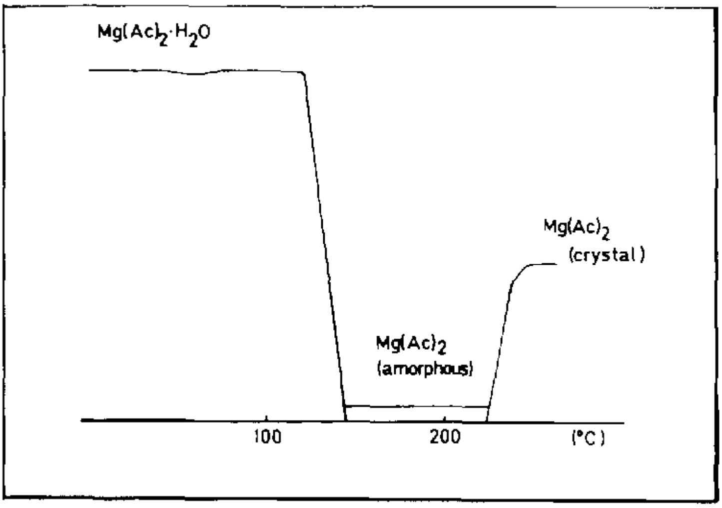

Fig. 9. High-temperature oscillating X-ray diffraction pattern of magnesium acetate monohydrate. Heating rate, 2°C min^{-1}; range of oscillation angle, 9.08° $< 2\theta <$ 13.91°; oscillation speed, 8° min^{-1}; X-ray source, Cu K_α, 80 mA and 40 kV; counting rate, 8×10^3 cps; time constant, 0.2 s.

CONCLUSIONS

In connection with the above-mentioned experimental results, the following conclusions may be drawn:

(1) under open and completely sealed conditions, dehydration of magnesium acetate tetrahydrate was a single-stage loss of water, but under quasi-sealed condition using 29.8, 60, and 100 $\mu m\phi$ tungsten wires, it was separated into two steps. Magnesium acetate monohydrate could be easily removed from the apparatus;

(2) as the amount of sample used for the present examination was small, the amount of intermediates was also small. It was thought to be difficult to take X-ray diffraction measurements using small sample sizes, however, this is made possible with the present method due to its greater power compared to the sealed X-ray generator. The intermediate was recognized as magnesium acetate monohydrate.

This method will be applied to various dehydration systems of some inorganic salts, especially those for which it is thought to be difficult to remove as intermediates.

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