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Note

THE THERMAL PHASE TRANSITION OF ANHYDROUS POTASSIUM OXALATE

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INTRODUCTION

Higashiyama and Hasegawa [1] studied the thermal phase transformation of anhydrous potassium oxalate by means of differential thermal analysis and thermogravimetry, together with the X-ray diffraction method. They reported the existence of three different anhydrous phases. The orthorhombic phase had the lattice parameters of $a = 10.9$, $b = 6.11$ and $c = 3.44$ Å at 17°C (Table 1) and was stable at room temperature. The tetragonal phase had the lattice parameters of $a = 7.01$ and $c = 7.53$ Å at 404°C (Table 1). This phase was irreversibly transformed from the above orthorhombic phase at 381°C and was stable at temperatures above 381°C until the beginning of the decomposition. The third phase appeared when the tetragonal phase was cooled to 215°C. However, Higashiyama and Hasegawa did not report the lattice parameters of the third phase.

In our previous paper [2] the thermal phase transformations of anhydrous rubidium and cesium oxalates were studied by means of thermal analysis and the X-ray diffraction method. We showed that three different anhydrous phases existed for both the oxalates, i.e. orthorhombic (**I**), orthorhombic (**II**) and tetragonal (**III**) phases as shown in Table 1, and that both the phase transitions (**I**) → (**II**) and (**II**) → (**III**) were reversible.

The existence of three phases and the reversibility of the phase transformation in both anhydrous rubidium and cesium oxalates were different from the results reported by Higashiyama and Hasegawa [1] for potassium oxalate.

In the present paper the thermal behavior of potassium oxalate is investigated in detail by means of thermal analysis and X-ray powder diffraction measurements at high temperatures. The results are compared with those of rubidium and cesium oxalates.

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EXPERIMENTAL

Potassium oxalate monohydrate (guaranteed reagent) was purchased from Wako Pure Chemical Industries (Osaka, Japan) Thermogravimetric (TG) and differential thermal analytic (DTA) curves were simultaneously recorded on a Rigaku-Thermoflex TG–DTA M 8075 About 20 mg of powder specimen was weighed into a platinum crucible and α-alumina was used as a reference material The enthalpy change for phase transformation was obtained from differential scanning calorimetric (DSC) curve recorded on a Shinku-Riko DSC-1500 M/L About 10 mg of specimen was placed in a platinum crucible and α-alumina was used as a reference material This instrument was calibrated with the heat of melting of indium ($\Delta H = 3\ 27$ kJ mol^{-1}, 156 5 °C) [3] and zinc ($\Delta H = 6\ 57$ kJ mol^{-1}, 419 6 °C) [2,3]

Powder X-ray diffraction patterns were obtained at various temperatures until 410 °C on a Rigaku-Diffactometer RAD-rA equipped with a standard high temperature sample holder [2] The specimen was heated at a rate of 2 °C min^{-1} and cooled at a rate of − 2 °C min^{-1} The sample chamber was

TABLE 1

Dimensions of the unit cell of $K_2C_2O_4$, $Rb_2C_2O_4$ [2], and $Cs_2C_2O_4$ [2]

Cell dimensions	$K_2C_2O_4\ H_2O$ [4]	$K_2C_2O_4$ (I)			$K_2C_2O_4$ (III)	
a (Å)	9 222	10 79	10 9 [1]		4 44	7 01 [1]
b (Å)	6 197	6 28	6 11 [1]			
c (Å)	10 690	3 52	3 44 [1]		6 36	7 53 [1]
β (°)	110 70					
Temperature (°C)	Room temp	190	17		395	404
Phase	Monoclinic	Orthorhombic			Tetragonal	

	$Rb_2C_2O_4\ H_2O$ [2]	$Rb_2C_2O_4$ (I)	$Rb_2C_2O_4$ (II)	$Rb_2C_2O_4$ (III)
a (Å)	9 68	3 69	4 56	4 59
b (Å)	6 35	6 60	6 54	
c (Å)	11 09	13 94	9 49	6 67
β (°)	109 4			
Temperature (°C)	20	330	385	405
Phase	Monoclinic	Orthorhombic	Orthorhombic	Tetragonal

	$Cs_2C_2O_4\ H_2O$ [2]	$Cs_2C_2O_4$ (I)	$Cs_2C_2O_4$ (II)	$Cs_2C_2O_4$ (III)
a (Å)	10 19	3 82	4 77	4 66
b (Å)	6 67	6 84	6 82	
c (Å)	11 44	14 44	9 95	7 04
β (°)	108 0			
Temperature (°C)	20	330	440	470
Phase	Monoclinic	Orthorhombic	Orthorhombic	Tetragonal

kept in vacuo (10^{-3} mmHg) during the measurement Cu $K\alpha$ radiation, nickel filter and a graphite monochrometer were used in all of the measurements The diffraction data were taken at a step of 0 02 deg width, and the diffraction peaks were indexed by use of a microcomputer, Sharp MZ-2000

RESULTS AND DISCUSSION

X-ray diffraction measurements

Figures 1A and 1B show the X-ray diffraction patterns of potassium oxalate monohydrate and of the anhydrous potassium oxalate obtained from its monohydrate by means of thermal dehydration at 106 °C, respectively This anhydrous salt was identified as an orthorhombic crystal having the lattice parameters $a = 10\ 79$, $b = 6\ 28$ and $c = 3\ 52$ Å at 190 °C, as shown by phase $K_2C_2O_4$ (**I**) in Table 1 The lattice parameters obtained are in satisfactory agreement with those reported by Higashiyama and Hasegawa [1] with due consideration for the difference between measuring temperatures

Figure 1C shows the X-ray diffraction pattern of the anhydrous potassium oxalate transformed from the orthorhombic phase (Fig 1B) by means of hold at the constant temperature of 395 °C in vacuo (10^{-3} mmHg) The diffraction peaks show that the orthorhombic phase (Fig 1B) transformed entirely to the tetragonal phase having the lattice parameters $a = 4\ 44$ and $c = 6\ 36$ Å at 395 °C as shown by phase $K_2C_2O_4$ (**III**) in Table 1 The lattice

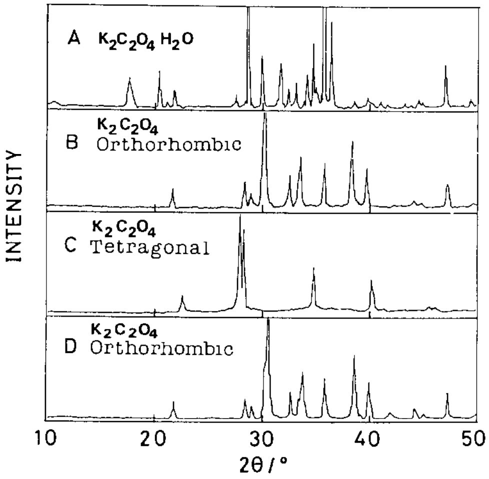

Fig 1 X-ray diffraction patterns of $K_2C_2O_4$ H_2O and $K_2C_2O_4$ A shows the pattern of $K_2C_2O_4$ H_2O B and C show those of $K_2C_2O_4$ measured at 190 and 395 °C, respectively D shows the pattern of $K_2C_2O_4$ preheated to 400 °C and then cooled to 190 °C

parameters obtained suggest that the present tetragonal phase corresponds to the tetragonal phases of $Rb_2C_2O_4$ (III) and $Cs_2C_2O_4$ (III) [2] (Table 1). The reason is that the cell dimensions of oxalates of the series tend to lengthen in the order $K_2C_2O_4 < Rb_2C_2O_4 < Cs_2C_2O_4$ in both the orthorhombic and tetragonal phases, though the cell dimensions are compared at different temperatures This finding seems to be due to the difference in the ionic radii of potassium, rubidium and cesium ions Therefore, the lattice parameters obtained were convincing on their values In ref 1 the lattice parameters $a = 7$ 01 and $c = 7$ 53 Å were given for the tetragonal phase at 404 °C

The X-ray diffraction pattern shown in Fig. 1D was obtained when the specimen in the tetragonal phase was cooled to 190 °C and held for 10 min The pattern was very similar to that of the orthorhombic phase shown in Fig 1B

The above findings suggest that the phase transition between the orthorhombic and tetragonal phases is reversible There was no evidence of the existence of a new phase and of an irreversible phase transition, as reported in ref 1

Differential scanning calorimetry of phase transition

Figure 2 shows the DSC curve of $K_2C_2O_4$ An endothermic peak was observed at 375 °C when the specimen was heated to 400 °C at heating rate 5 °C min^{-1} When the specimen preheated to 400 °C was cooled to 280 °C,

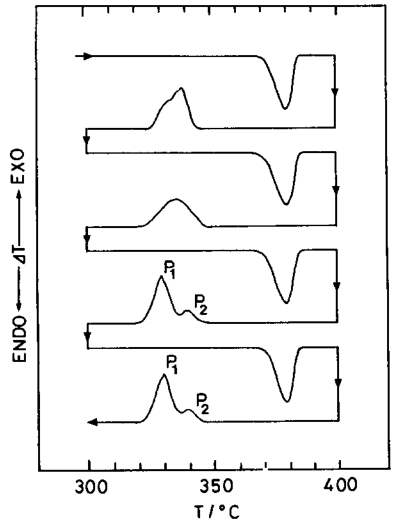

Fig 2 Heating and cooling DSC curve of $K_2C_2O_4$ DSC measurements were performed in vacuo (3 mmHg)

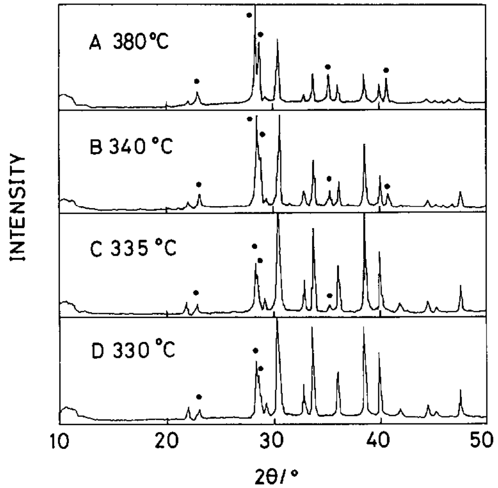

Fig 3 X-ray diffraction patterns of $K_2C_2O_4$ measured after three repeats of the heating and cooling cycle (290–395 °C) A, 380, B, 340, C, 335, and D, 330 °C The peaks marked with ● belong to the tetragonal phase, and the unmarked peaks to the orthorhombic phase

an exothermic peak accompanying a shoulder was observed around 338 °C The values for enthalpy changes calculated from the endothermic peak on heating and from the exothermic peak on cooling were equal to 19 1 kJ mol^{-1} in their absolute values. This confirms the preceding suggestion that the phase transition between the orthorhombic phase (**I**) and the tetragonal phase (**III**) was reversible When the heating and cooling cycle was repeated three times in the range 290–395 °C, the exothermic peak was nearly separated into two peaks, P_1 and P_2 observed at 330 and 340 °C, respectively, as shown in Fig. 2 The enthalpy changes for the peaks of P_1 and P_2 were − 15 5 and − 3.6 kJ mol^{-1}, respectively, and the sum of these values was − 19.1 kJ mol^{-1} The separation of the exothermic peak suggests the existence of another phase between the orthorhombic phase (**I**) and the tetragonal phase (**III**) as reported for rubidium and cesium oxalates [2]. In order to confirm the existence of the new phase, X-ray diffraction measurements of the specimen were taken in detail after the heating and cooling cycle repeated three times in the range 290–395 °C The diffraction patterns of specimens were measured at intervals of 5 °C (increasing temperature) around the endothermic peak (365–410 °C)

Figure 3A is a typical diffraction pattern measured at 380 °C The figure shows that the diffraction peaks could be identified as the mixture of tetragonal and orthorhombic phases, and that at 380 °C the oxalate was in the course of transition from the orthorhombic to the tetragonal phase

The diffraction patterns were also measured at intervals of − 5 °C (decreasing temperature) around the exothermic peaks (410–300 °C) Figures. 3B, 3C and 3D show the variation of the diffraction patterns measured at

340, 335 and 330 °C, respectively The patterns could be also identified as the mixture of tetragonal and orthorhombic phase The figures clearly show that the ratios of tetragonal phase to orthorhombic phase varied with decreasing temperatures in the course of the phase transition There was no existence of a new phase such as the orthorhombic phase (**II**) reported for rubidium and cesium oxalates [2] The separation of the exothermic peak suggests that the orthorhombic phase (**II**) would be in existence as a seed even if it could not be confirmed experimentally

CONCLUSIONS

Orthorhombic crystals of anhydrous potassium oxalate were obtained from the thermal dehydration of potassium oxalate monohydrate The crystals transformed into the tetragonal phase at 395 °C The phase transition between these two phases was reversible

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