Thermochimica Acta, 83 (1985) 173–179
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

A STUDY OF THE POLYMORPHISM OF POTASSIUM NITRATE STARTING FROM ROOM TEMPERATURE AND AT ATMOSPHERIC PRESSURE

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(Received 23 July 1984)

ABSTRACT

We expose in this paper the results of the temperature and enthalpy change measurements for the transformations II → I, I → III, III → II and III → I. These results were obtained by the DTA technique and correspond to various thermal cycles that are characterized by the initial and final temperatures. The method used has clarified several points such as how the thermal treatment and the humidity in the sample influence the transition I → III and the conditional apparition of phase III on cooling.

INTRODUCTION

The transitions of potassium nitrate through the three phases in which it is found from room temperature to melting point have been the subject of diverse thermal, electrical and structural studies. The ferroelectric behaviour of phase III has particularly increased the interest of such transitions, which generally involve specific enthalpy changes and evolve depending on the thermal treatment used.

According to the literature on thermal studies made by DTA and DSC [1–7] it is observed that an endothermic peak appears at about 128°C when the potassium nitrate is first heated. It corresponds to a structural change from orthorhombic (phase II) to trigonal (phase I), with an enthalpy variation of about 54 J g^{-1}. On cooling the sample from phase I an exothermic peak is obtained around 125°C with an enthalpy change that ranges from 20 to 25 J g^{-1}, together with another one of very irregular shape [2,6] that appears at a lower and variable temperature or with an exothermic displacement of the baseline. This second exothermic peak is not always obtained

0040-6031/85/$03.30

and its existence is conditioned to the maximum temperature to which the salt has been exposed in phase I before cooling [1,2,4–8]. It appears at lower temperatures when the temperature previously reached is higher.

Reheating the KNO_3 gives again an endothermic peak at the same temperature (128°C), or advanced 1 or 2°C, with an enthalpy change that is equal to or smaller (even to half) than that in the first heating process. The variations in temperature and change of enthalpy in the endothermic process seem to depend on the lowest temperature from which the reheating begins [2,9] and the time for which the salt has remained at it [2].

EXPERIMENTAL

Sample masses around 30 ± 0.2 mg of KNO_3 were used with a minimum purity of 99% (Merck pro analysi). The size of the grains was within 60–100 μm. After each experiment a mass loss of 0.2–0.4 mg, which corresponds to 1% of the total mass, was observed, which was assumed to be related to the loss of humidity in the sample. The sample reference compound was SiC, which is inert in this temperature range, and ~ 35 mg cylindical aluminium crucibles were used. All experiments were made in a static air atmosphere. The furnace used presents a great thermal resistance between the alveoles, each of which contained three chromel–alumel thermocouples in serial disposition allowing a differential signal with a sensitivity varying between 5 and 4 mV W^{-1} in the range between 50 and 250°C, respectively. The ΔT signal has been amplified by a factor of 5×10^3–8×10^4.

The typical heating rate was 5°C min^{-1}. However, it was not possible to control the cooling rate rigorously, because the equipment lacked a cryogenic system, and it was therefore between -3 and -1°C min^{-1}.

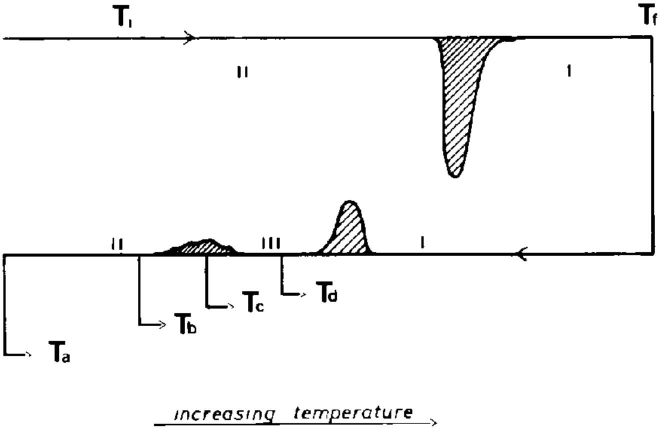

Fig 1. Scheme of the thermal cycles carried out.

The areas of the peaks were measured three times with a Coradi planimeter (resolution 16×10^{-3} mm^2). The present study is based on the scheme shown in Fig. 1.

The final temperature on heating, T_f, was

$130°C < T_f < 170°C$ $200°C < T_f < 333°C$

$170°C < T_f < 200°C$ $T_f > 333°C$ (melting point of KNO_3)

The initial temperature before heating, T_i, was chosen to give potassium nitrate in the following forms:

(1) Phase II (at room temperature, T_a);
(2) Phase II (at a temperature greater than room temperature, T_b);
(3) Coexistence of phases II and III (T_c);
(4) Phase III (T_d).

Eighteen runs were carried out, each with different thermal cycles between T_i and T_f. All the temperature and enthalpy variation values presented here are the average of 10 to 40 measurements.

EXPERIMENTAL RESULTS

An endothermic peak is obtained at about 132°C when first heating the potassium nitrate, representing the process II → I, with an area we will refer to as S. On cooling, two first-order exothermic processes appear, the first one around 125°C, corresponding to the transition I → III, with an area $0.47S$, and the second one always at lower temperatures, interpreted as the transformation III → II. It is displayed as a peak of very irregular shape and is found at a temperature dependent on T_f, at which the KNO_3 has begun to cool down in phase I. These three thermal phenomena can be observed in Fig. 2.

The process III → II occurs at a lower temperature, after heating to T_f, as long as the potassium nitrate is not brought to melting point. If $T_f > 333°C$ then the said transition is seen as a much stronger and thinner signal and at a higher temperature than when the sample has not been previously melted, but in any of the two cases the average area of the peak is $0.42S$. This process was always present irrespective of T_f.

When reheating the potassium nitrate from room temperature (T_a in Fig. 1), at which it stayed for 12 h, the endothermic peak is of area S but appears at 129 instead of 132°C. On this same second heating cycle the endothermic transition II → I is seen to be identical to the transition II → I in the first cycle, if the second one begins at a temperature higher than T_a (T_b in Fig. 1).

If the reheating begins from T_c (coexistence of phases II and III) then the endothermic process gives an area equal to the area of the first added to a fraction of the area of the second exothermic processes, the peak appearing around 132°C.

When the KNO_3 was reheated from phase III (T_d in Fig. 1) an endothermic peak of $0.50S$ was obtained, corresponding to the III → I process, around 132°C.

The II → I transition of KNO_3 was used as a calibrating point for the experimental system [9] and a value of 53.5 J g^{-1} has been ascribed to its area S because of the diverse values of ΔH corresponding to this process found in the literature [2,4,5,7]; this value is better adjusted to the variation of the calibration factor with temperature in the present case.

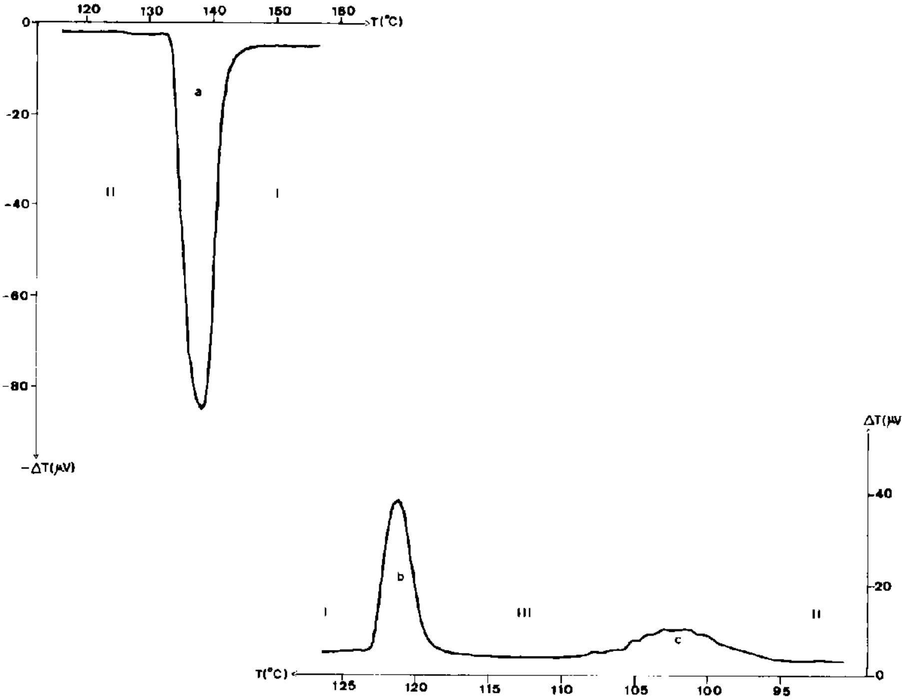

Fig. 2. Processes II → I (a), I → III (b) and III → II (c) for $T_i = T_a$ and 130°C < T_f < 170°C.

TABLE 1

Extrapolated onset temperatures and ΔH corresponding to the transitions of the potassium nitrate

Transition	Ext. onset temp. (°C)	ΔH (J g^{-1})
II → I	132 or 129 ± 1 [a]	53.5 ± 3%
III → I	132 ± 1	26.7 ± 3%
I → III	122 ± 1	−25.2 ± 3%
III → II	between 111 and 70 [a]	−22.5 ± 6% [b]
III → II		−26.8 or −28.3 ± 9% [c]

[a] Depending on the thermal treatment.

[b] Direct measurement of the peak's area.

[c] Differences in ΔH between the process II → I and III → I or I → III, respectively.

The extrapolated onset temperatures of the cycles and the energies corresponding to each transition studied are given in Table 1.

DISCUSSION

The addition of the ΔH values of the exothermic processes represents only 89% of the corresponding one in the process II → I. Harmelin [2] imputed this fact to the incompleteness of the process III → II, therefore implying that some KNO_3 is present in phase III in a metastable form even at room temperature. The complete transformation into phase II is not fulfilled until some time has passed at this temperature. We have seen that the area of the endothermic peak is the same independent of which has been the initial temperature (T_a or the higher T_b) when reheating the potassium nitrate from phase II. It has been found in this way that is not necessary to allow the salt to remain at room temperature for a length of time to find the whole area S of the process II → I on heating, in agreement with Garn et al. [6].

However, this 11% difference cannot, according to our results, only be imputed to the process III → II because the processes I → III and III → I, theoretically reversible, give a difference in ΔH of 7% which can be detected by our experimental system in this temperature range. We therefore think that not only is the coexistence of phases III and II possible but also coexistence between phases I and III when the salt is at a temperature between the two exothermic processes.

Since when the salt is heated up from T_c the area of the endothermic peak is found equal to the addition of that belonging to the first exothermic peak and the fraction of that corresponding to the second exothermic peak in the previous cooling, it is possible to say that the transition II → I is made through the ferroelectric phase. We have also observed a maximum in the permitivity in monocrystals of KNO_3 at around 130°C, a result that agrees with Sawada et al. [10,11].

Some authors [2,5,6] note that the process III → I begins 1 or 2°C before the II → I transition. It has not been possible to detect any difference in this work and we think it is due to the similarity of phases I and III, which are both trigonal and have close spacial groups [12–15], and therefore make the transition easy. On the other hand, the process II → III should theoretically begin earlier but it is slower, since the crystalline structures are different: orthorhombic and trigonal, respectively.

The two exothermic processes were always found on cooling, independent of the value of T_f and of the number of previous thermal cycles, which contradicts other papers that impute the appearance of phase III to the lack of humidity in the sample [1–4,7].

The values of ΔH of the distinct processes in relation to the above accepted value of 53.5 J g^{-1} for the transformation II → I are shown in

TABLE 2

ΔH (J g^{-1}) for some transitions of KNO_3 according to the literature (values between parentheses indicate measurements by DSC)

II → I	III → I	I → III	III → I	Ref.
55.2	–	−28.5	–	2
49.4	25.0	−25.2	–	4
48.6	22.5 (22.5)	−23.4 (−23.1)	−10.8	5
53.5	–	−29.9	−23.6	7

TABLE 3

Quotients between the ΔH of process II → I with III → I and I → III, respectively

$\dfrac{\Delta H(\text{II} \to \text{I})}{\Delta H(\text{III} \to \text{I})}$	$\dfrac{\Delta H(\text{II} \to \text{I})}{\Delta H(\text{I} \to \text{III})}$	Ref.
1.98	−1.96	4
2.16	−2.08 (−2.10)	5
–	−1.94	2
–	−1.79	7
2.00	−2.12	This work

Table 2 for comparison with the values given in the literature.

These values are quite close to those obtained in this work, as can be seen from Table 3.

CONCLUSIONS

We infer that there is a thermal hysteresis in the transitions: (a) II → I, as a function of the temperature from which the heating begins in phase II; (b) III → II, as a function of the temperature from which the cooling begins in phase I.

It has been seen that the KNO_3 in phase III can be completely changed into phase II without the need to be brought down to room temperature, in agreement with Garn et al. [6]. The difference between ΔH in process II → I with I → III and III → II cannot only be imputed to the second exothermic peak.

The appearance of phase III on cooling has been proved independent of the humidity contained in the sample, since it is always found, regardless of how many times the sample has been thermally cycled before.

We have calculated the extrapolated onset temperatures and ΔH values related to all the processes and particularly III → II making direct use of the peak's area.

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