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Thermochimica Acta 293 (1997) 167–170

thermochimica acta

# Thermobarometric study of $KNO_3$ phase transitions

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Received 26 June 1996; received in revised form 19 November 1996; accepted 11 December 1996

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**Abstract**

In this work, a thermobarometric study of bulk $KNO_3$ submitted to pressure less than 150 MPa has been performed by means of the Metabolemeter system. The effect of pressure on the transitions between the different phases I, II and III have been analysed. Endothermic transformation from II to I takes place through phase III. On cooling from phase I, a coexistence between the phases II and III, metastable at room temperature, is always obtained. © 1997 Elsevier Science B.V.

*Keywords:* Potassium nitrate; Phase transitions; Thermobarometric measurements; Metastability; Molar volume

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## 1. Introduction

The polymorphism [1,2] of $KNO_3$ at atmospheric pressure has been extensively studied. $KNO_3$ exists in three solid phases: Phase II (orthorhombic, space group P*mcn*, $Z=4$) which transforms upon heating to phase I (rhombohedral space group R3*m*, $Z=1$) at approximately 403 K, and a ferroelectric form (phase III) obtained when cooling phase I. Phase III is also rhombohedral, space group R3*m* and $Z=1$, showing spontaneous polarization along the *c* axis [3]. Ferroelectric $KNO_3$ films may be used for fabricating memory devices [4]. Heating phase III, form I is obtained again. Both II→I and III→I order–disorder transitions are initiated by rotations of $NO_3^-$ ions about the *c*-axis. Lattice-dynamics calculations [5] reveal that these rotations are connected with the abnormally large thermal expansions found in the *c*-axis direction [2].

Some studies on $KNO_3$ polymorphism are not in agreement with the formation of phase III [6–9]. These studies point out that the temperature range of existence of phase III depends on many factors: thermal history, purity level, absence of moisture, sample geometry etc. Generally, it is accepted that thin-film $KNO_3$ exhibits ferroelectric behavior at much lower temperatures than bulk material [10]. Little information can be found about $KNO_3$ transitions under pressure. Bridgman's phase diagram [11] shows that hydrostatic pressure greatly increases the temperature range of form III. Davis and Adams [12] determined the transition rates of $KNO_3$ under pressure by means of X-ray measurements.

The aim of the present work is to contribute to the knowledge of $KNO_3$ polymorphism. The characterization of the phase transitions is performed using a Metabolemeter device. For the past ten years this apparatus is being used to the study of phase transitions under pressure, basically in liquid mesophases. The principle of this thermobarometric technique is the measurement of the pressure variations versus

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*PII* S0040-6031(97)00024-5

temperature of a sample enclosed in a rigid-metallic cell.

## 2. Experimental

We used $KNO_3$, purchased from Aldrich (99.5% purity), without further purification. The polymorphism has been studied under pressure by the M.T.M. Leader Metabolemeter [13]. The transition temperature has been related to the pressure by the Clapeyron equation:

$$\frac{dP}{dT} = \frac{\Delta H}{T \Delta V}$$

where $\Delta H$ and $\Delta V$ are the enthalpy and the molar volume changes in the transition.

The evolution of the pressure of a sample placed in a 20 $mm^3$ cell has been measured with a piezoresistive gauge. A scanning rate of 2 K $min^{-1}$ has been used. The upper temperature limit of the Metabolemetre is 500 K. The lower pressure increment that can be detected at a first-order transition is about 0.5 MPa and the lower slope change is approximately 0.1 MPa $K^{-1}$.

## 3. Results and discussion

The ferroelectric phase is always obtained from cooling form I and it is accepted as metastable at atmospheric pressure [5,9,14]. The temperature range of existence of phase III depends on the thermal treatment applied to the sample. DSC curves in Figs. 1 and 2, obtained in a Setaram DSC92 with sample masses of 100 mg and scanning rates of 2 K $min^{-1}$, show the well-known behavior of powder $KNO_3$ at atmospheric pressure.

As can be seen in Fig. 2, conversion of phase III to form II is detected when the sample is cooled from the liquid state. Melting increases the compactness of the sample and the III→II reversion takes place more easily. According to the literature, III to II transformation may be partial and the coexistence of both phases is possible during a period of few hours at room temperature [6,9,12,15].

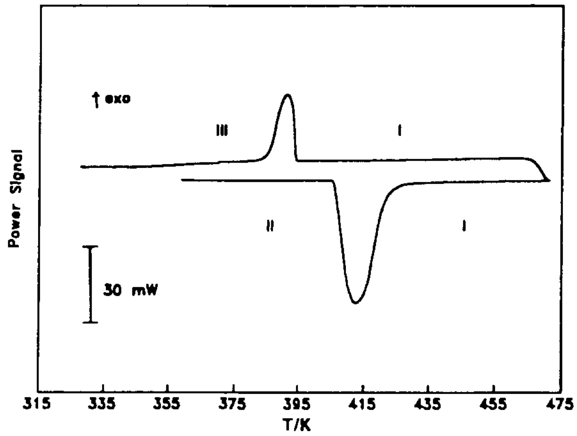

Fig. 1. DSC curve corresponding to the transitions II→I and I→III of a $KNO_3$ powdered sample.

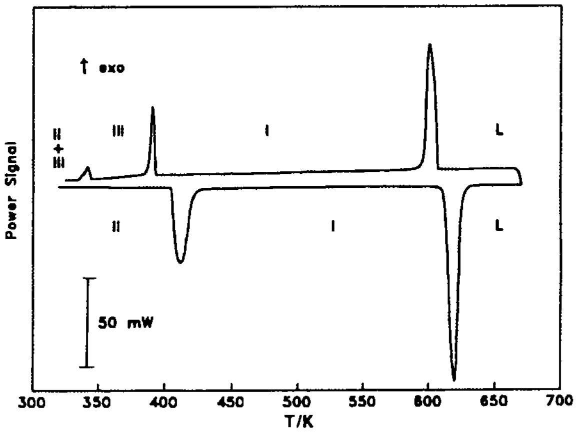

Fig. 2. DSC curve of $KNO_3$ cycled from room temperature to the liquid state.

With our thermobarometric device we have submitted $KNO_3$ to different thermal cycles. Taking into account the pressure limit of the Metabolemetre is 150 MPa, we have applied to the sample an initial pressure in the range between 20 and 60 MPa. In Fig. 3, we represent the thermobarogram of a thermal cycle from room temperature to 440 K (phase I). On heating, we can see at approximately 400 K a diminution of the pressure corresponding to a decrease of molar volume, according to the Clapeyron equation. This is followed in the thermobarogram by an increase of pressure. The first effect is attributed to the II→III process and the second one to the III→I.

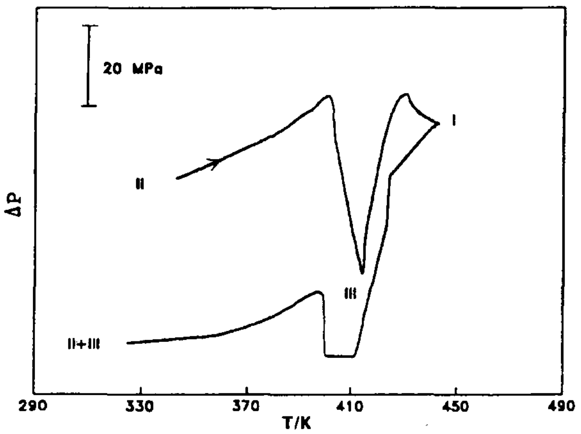

Fig. 3. $KNO_3$ thermobarogram of a sample cycled until 440 K (phase I).

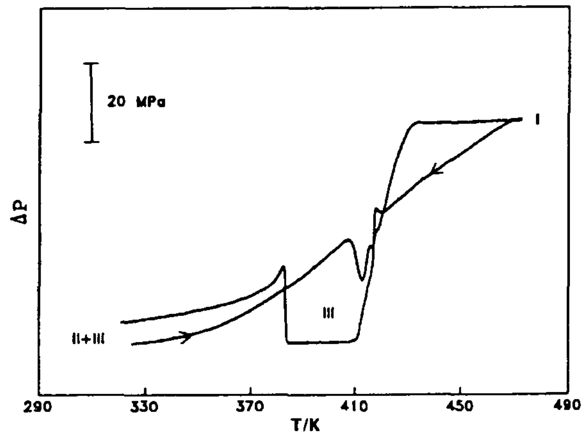

Fig. 4. $KNO_3$ thermobarogram of a sample cycled until 480 K (phase I).

The slopes of both processes are very similar with an average absolute value about 4 MPa $K^{-1}$. Accepting that the enthalpy change of the complete II→III transition is about 50% of II→I [4,15] and from Clapeyron equation, taking the value of 77.5 Å$^3$ for the molecular volume of phase III at 393 K [14], we have obtained differences of 4% between the molar volume of phase III and those of phases I and II. From crystallographic measurements [1,2,14] this difference is about 5%.

The sharp diminution of pressure observed in this figure, on cooling phase I, corresponds to the I→III transition taking place at the same temperature as the III→I transformation. The increase of pressure at about 400 K is attributed to the process III→II. This jump is clearly smaller than that of II→III on heating, so we assume that the transformation of the ferroelectric phase is not complete. In Fig. 4, we show the thermal cycle of the sample obtained after the cooling represented in Fig. 3. At the beginning of the heating there is a coexistence of phases II and III, so we observe in Fig. 4 only a small diminution of pressure at 400 K. We have verified that the coexistence of II and III phases at room temperature occurs for several days. Reversion of ferroelectric form to phase II is clearly dependent on the thermal history: The temperature range of phase III on cooling is broadened while the temperature reached in phase I is higher (see Figs. 3–5). This fact has been already observed in DSC measurements at atmospheric pressure [6,16].

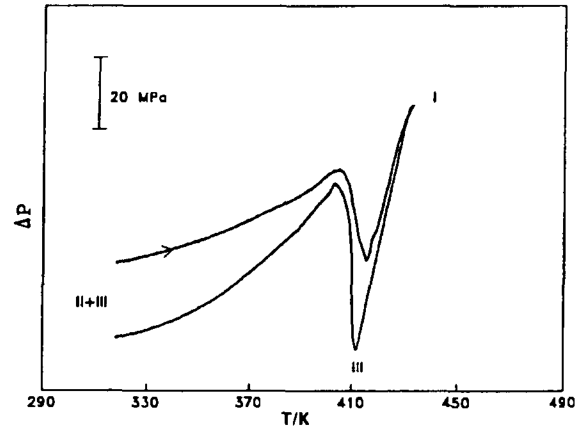

Fig. 5. $KNO_3$ thermobarogram of a sample cycled until 430 K (phase I).

However, as we can see in Fig. 6, if $KNO_3$ is heated to a temperature lower than that of the beginning of III→I process, the II↔III transition is reversible.

$\Delta P$ values at the beginning of the thermal cycles represented in Figs. 4–6 are not coincident due to the application of different initial pressures to the sample. The quantity of phases II and III that coexists at room temperature is not the same; this fact causes differences between initial and final $\Delta P$ values in these cycles. Taking into account that the molar volumes of phases II and I are very similar, the pressure levels before II→III and after III→I transitions are very similar, as we can see in Fig. 3. However, the differences in these levels, observed in the thermal cycles

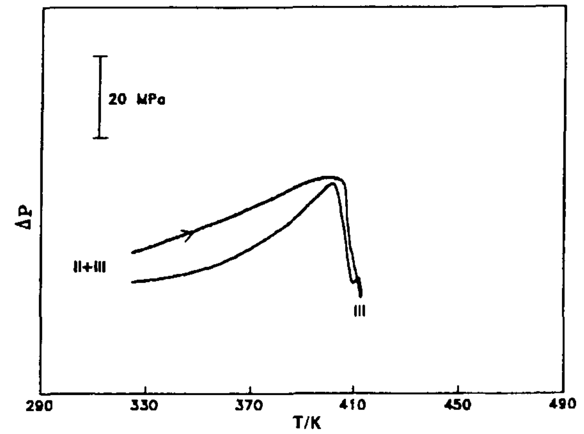

Fig. 6. $KNO_3$ thermobarogram of a sample cycled until 410 K (phase III).

represented in Figs. 4 and 5, are due to the coexistence of phases II and III.

## 4. Conclusions

In this work we have presented the first results of $KNO_3$ phase transitions obtained by the Metabolemeter device. This quantitative method allows one to measure, versus temperature, the pressure of a small quantity of sample enclosed in a rigid cell, using only intensive data.

The present study contributes to the comprehension of the $KNO_3$ polymorphism. The existence of a ferroelectric form, as a metastable phase at room temperature and atmospheric pressure, is a well-known result. At higher pressures and temperatures this phase is stable [11]. Form III can be kept at room temperature, coexisting with the stable phase II, for several hours. X-ray studies reveal that, on heating at atmospheric pressure, phases I and III grow simultaneously at the expense of phase II, and thereafter phase III disappears. However conversion of II→III is never detected using the DSC technique, working at atmospheric pressure.

Our thermobarometric measurements, performed with pressures less than 150 MPa, show that there are two processes on heating phase II: the II→III transformation, involving a diminution of volume, which is followed by the III→I conversion giving rise an increase of volume. On cooling from phase I, a partial reversion of phase III to II is obtained so, both phases, II and the remaining ferroelectric, coexist at room temperature for several days. This enlargement of the period of coexistence of phases II and III is due to the increase of the pressure. The volume changes between these phases obtained from our macroscopic measurements are in agreement with those determined from crystallographic data.

## Acknowledgements

This work has been supported in part by the CICYT (Project PTR94-049).

## References

[1] S. Swaminathan and S. Srinivasan, Acta Cryst., A31 (1975) 628.
[2] J.K. Nimmo and B.W. Lucas, Acta Cryst., B32 (1976) 1968.
[3] S. Sawada, S. Nomura and Y. Asao, J. Phys. Soc. Jpn., 16 (1961) 2486.
[4] J. Isaac and J. Philip, J. Appl. Phys., 69 (1991) 7765.
[5] H.M. Lu and J.R. Hardy, Phys. Rev. B, 44 (1991) 7215.
[6] M. Harmelin, J. Thermal Anal., 4 (1972) 403.
[7] P.D. Garn, B.I. Diamonstone and O. Menis, J. Thermal Anal., 6 (1974) 623.
[8] V.V. Deshpande, M.D. Karkhanavala and U.R.K. Rao, J. Thermal Anal., 6 (1974) 613.
[9] M.J. Westphal, J.W. Wood, R.D. Redin and T. Ashworth, J. Appl. Phys., 73 (1993) 7302.
[10] J.F. Scott, M.S. Zhang, R.B. Godfrey, C. Araujo and L. McMillan, Phys. Rev. B, 35 (1987) 4044.
[11] F. Rapoport and G.C. Kennedy, Phys. Chem. Solids, 26 (1965) 1995.
[12] B.L. Davis and L.H. Adams, J. Phys. Chem. Solids, 24 (1963) 787.
[13] J.M. Buisine, B. Soulestin and J. Billard, Mol. Cryst. Liq. Cryst., 91 (1983) 115.
[14] K.O. Strømme, Acta Chem. Scand., 23 (1969) 1625.
[15] J. Muntasell, J. Navarro and E. Cesari, Thermochim. Acta, 83 (1985) 173.
[16] C. Mazières, Ann. Chim. (1961) 598.