Melting Curve of $NaClO_3$ to 42 kbar

A. B. WOLBARST, J. B. CLARK, and P. W. RICHTER
National Physical Research Laboratory,
Pretoria 0001, South Africa

(Z. Naturforsch. **31 b**, 1005–1006 [1976]; received April 20, 1976)

Melting Curve, High Pressures

The melting curve of $NaClO_3$ was determined to 42 kbar. The equation

$$t_m\,(°C) = 270 + 15.09\,(P\text{-}0{,}85) - 0.4044\,(P\text{-}0.85)^2 + 0.004555\,(P\text{-}0.85)^3$$

fits the data with a standard deviation of 5 °C.

RAPOPORT[1] determined the phase diagram of $NaClO_3$ to 40 kbar. Recently SCHAMM and TÖDHEIDE[2] redetermined the melting curve in a hydrostatic device to 5 kbar, and found a new triple point at 0.85 ± 0.1 kbar, 270 ± 2 °C. From this triple point the true melting curve rises steeply, indicating that what was previously[1] reported as the melting curve is, in fact, a solid-solid phase boundary. RAPOPORT'S[1] technique was not suited to precise measurements below a few kbar, and hence it is understandable that he did not observe the true melting curve.

Merck G. R. grade $NaClO_3$ with a minimum stated purity of 99% was used. Pressures were generated using a piston-cylinder device[3,4], and melting was detected by differential thermal analysis (DTA) using chromel-alumel thermocouples. The experimental technique has been described elsewhere[5,6].

Multiple temperature cycling at constant pressure produced severe depression of the melting point, and therefore single-shot experiments were performed, where only the initial melting signal was used. Samples were contained in niobium capsules and post-mortem analysis showed no niobium contamination after the single melting cycle.

Metastable phases can be crystallized from the melt[7], and it is possible that many of the present experimental problems experienced are due to the formation of these metastable phases. The practice of using only the first melting signal obtained ensures that the melting curve reported is that of pure $NaClO_3$.

Friction corrections were estimated by comparison with the hydrostatic data[2] and previous experimental experience in this p-T range. The present results are believed to be accurate to ± 1 kbar.

The complete phase diagram of $NaClO_3$ is shown in Fig. 1. The melting curve can be described by the equation

Requests for reprints should be sent to Dr. J. B. CLARK, National Physical Research Laboratory, P. O. Box 395, *Pretoria 0001*, South Africa.

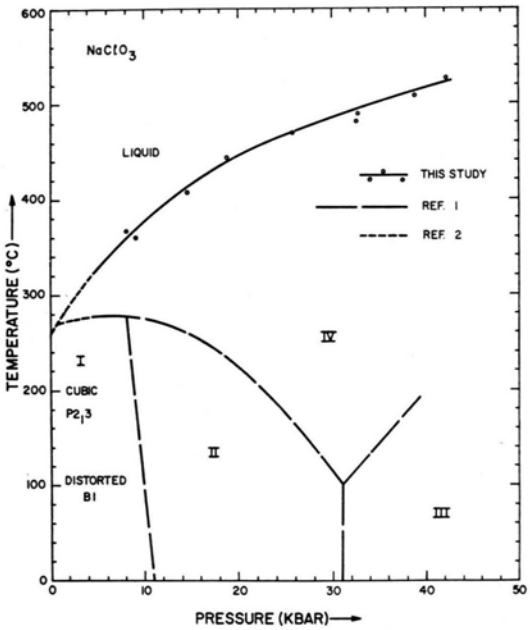

Fig. 1. Phase diagram of $NaClO_3$ to 42 kbar.

$$t_m\,(°C) = 270 + 15.09\,(P\text{-}0.85) - 0.4044\,(P\text{-}0.85)^2 + 0.004555\,(P\text{-}0.85)^3$$

with a standard deviation of 5 °C.

The previous[1] discussion of the disappearance of the DTA signals obtained on the II/IV boundary is now inappropriate. The increasing hysteresis obtained on this boundary must be attributed to increasing sluggishness with increasing pressure and decreasing temperature, in good agreement with BRIDGMAN'S[8] original results. This increasing sluggishness would automatically broaden DTA signals and eventually make them unobservable.

The relationship between the I, II and IV phases is of interest*. $NaClO_3$ I is initially more dense than $NaClO_3$ IV, and the I/IV boundary rises gently. $NaClO_3$ IV would appear to be exceptionally compressible; consequently it becomes denser than both $NaClO_3$ I and $NaClO_3$ II at high pressures.

$NaClO_3$ I has a distorted B1 structure, and there should also exist a B2-related phase, as in the case[10] of $KClO_3$. The volume changes associated with the I/II and II/III transitions, however, are too small to suggest that either $NaClO_3$ II or III is the expected B2-related phase. By comparison with the simpler alkali halides, cyanides, nitrites, nitrates, *etc.*, we expect the B1/B2-related transition to occur at pressures substantially higher than 40 kbar.

The authors would like to thank Prof. W. KLEMENT, Jr. for stimulating discussions, and Mrs. L. DU TOIT for assistance with technical work. Mr. A. J. DE KLEYN

* VIJAYA *et al.*[9] have recently observed the I–II transition by means of nuclear quadrupole resonance

and his staff, and Mr. J. J. ERASMUS and his staff were responsible for keeping the piston-cylinder in good repair and for the manufacture of the furnace parts. Calculations were carried out on the IBM 370/158 of the National Research Institute for Mathematical Sciences.

[1] E. RAPOPORT, J. Chem. Phys. **46**, 3279 [1967].
[2] R. SCHAMM and K. TÖDHEIDE, personal communication.
[3] G. C. KENNEDY and R. C. NEWTON, in "Solids under Pressure" (W. PAUL and D. M. WARSCHAUER (eds)), McGraw-Hill, New York 1963.
[4] G. C. KENNEDY and P. N. LAMORI, in "Progress in Very High Pressure Research" (F. P. BUNDY, W. R. HIBBARD, and H. M. STRONG (eds)), p. 304, Wiley, New York 1961.
[5] C. W. F. T. PISTORIUS and J. B. CLARK, High Temp. High Press. **1**, 561 [1969].
[6] P. W. RICHTER and C. W. F. T. PISTORIUS, J. Solid State Chem. **3**, 197 [1971].
[7] P. MEYER, Bull. Soc. fr. Minéral. Cristallogr. **95**, 541 [1972]; P. MEYER and M. GASPERIN, Bull. Soc. fr. Minéral. Cristallogr. **96**, 18 [1973].
[8] P. W. BRIDGMAN, Proc. Am. Acad. Sci. **72**, 45 [1937].
[9] M. S. VIJAYA, J. RAMAKRISHNA, A. S. RESHAMWALA, and A. JAYARAMAN, Mat. Res. Bull. **7**, 615 [1972].
[10] C. W. F. T. PISTORIUS, J. Chem. Phys. **56**, 6263 [1972].