

High-Pressure Phase Research on Nb₂O₅

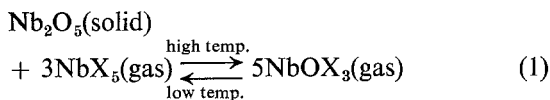
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Experimental results indicate that the direct transitions from the H form to the T form and from the H form to the B form of Nb₂O₅ are possible under high pressures. Both highly pure and less pure reagents were used. The distinct TT form was obtained only when less pure reagents were used so that the TT form seems to be stabilised by means of trace impurities. Previously the TT form was indexed as having a pseudo-hexagonal unit cell. However, the present distinct TT form has a monoclinic unit cell, $a = 7.23$ Å, $b = 15.7$ Å, $c = 7.18$ Å, $\beta = 119^\circ 5'$, $V = 711.7$ (Å)³. Eight molecules are contained per cell. Probably only B, T and H have stable regions; the other polymorphs of Nb₂O₅ may be metastable forms or forms stabilised by impurities.

1. Introduction

It has been shown by previous work [1-13] that Nb₂O₅ appears in several polymorphs, such as N, R, P, H, M, T, TT, B, etc., according to the notation adopted by Brauer and Schäfer. Structural investigations of P [18], B [7], R [15], N [18], H [14], and M [21] forms have been reported. Many of these forms have been synthesised by means of chemical transport methods:



where X = Cl, I, Br. Samples obtained by chemical transport methods contain a small proportion of halogen.

Schäfer *et al* stated that the forms of Nb₂O₅ prepared at lower temperatures are mostly metastable [20]. Phase transitions obtained so far are listed in table I. For a phase to be the stable form it is necessary to show under certain conditions that reversible transitions are observable. The purpose of the present study is to consider the relationships between the polymorphs by using high-pressure techniques.

2. Experimental Procedure

2.1 Preparation of Reagents

High-purity Nb₂O₅, "spectrographically standardised", was obtained from Johnson Matthey Chemicals Ltd. The composition of this material

is listed in table II. The sample was heated at 1230°C for 96 h in a platinum boat to ensure complete conversion to the H form. The other reagents used were less pure.

2.2. Calibration of Pressure Scale

The pressure calibration was done by means of the transitions: Bi I-II at 25.5 kb, Bi II-III at 28.0 kb, Tl II-III at 34.6 kb, Ba at 55 kb, Bi IV-V at 77.3 kb, and Ba at 144 kb.

2.3. Piston-cylinder Type Apparatus

A piston-cylinder type apparatus was used for generating the pressure, ranging from ~5 to ~20 kb. The pressure-transmitting-medium was molten glass. The pressure scale below a few kb seemed to be unreliable. The experimental arrangement of the piston-cylinder type apparatus is shown in fig. 1. Chromel-alumel thermocouples and Pt-Pt Rh_{0.13} thermocouples were used for measuring temperature.

2.4. Belt-type Apparatus

A "belt"-type apparatus was used for generating pressures in the range of ~30 to ~60 kb. Temperatures were known from the power-temperature calibration curve obtained previously. The experimental arrangement of the "belt"-type apparatus is shown in fig. 2.

2.5. Bridgman-type Apparatus

The Bridgman anvil used was of the internal

TABLE I Phase transitions previously obtained.

Brauer [1]	amorphous $\xrightarrow{600^\circ\text{C}}$ T $\xrightarrow{850^\circ\text{C}}$ M $\xrightarrow{1050^\circ\text{C}}$ H
Shafer and Roy [13]	III $\xrightarrow{380^\circ\text{C}}$ II $\xrightarrow{1060^\circ\text{C}}$ I $\xrightleftharpoons{1285^\circ\text{C}}$ I-high*
Holtzberg and Reisman [5]	amorphous $\rightarrow \gamma + \gamma' \xrightarrow{830^\circ\text{C}} \alpha + \alpha'$
Taylor and Doyle [19]	NbO ₂ $\xrightarrow{600-850^\circ\text{C}}$ $\gamma \xrightarrow{700-800^\circ\text{C}}$ α
Terao [9, 10]	NbO $\xrightarrow{550^\circ\text{C}}$ $\delta \xrightarrow{400-700^\circ\text{C}}$ $\gamma \rightarrow \gamma' \xrightarrow{750-900^\circ\text{C}}$ $\beta \rightarrow \alpha$
Schäfer <i>et al</i> [20]	amorphous $\xrightarrow{500-600^\circ\text{C}}$ TT $\xrightarrow{600-800^\circ\text{C}}$ T $\xrightarrow{850^\circ\text{C}}$ H $\xrightarrow{850-900^\circ\text{C}}$ M $\xrightarrow{900^\circ\text{C}}$ H
	amorphous $\xrightarrow{850^\circ\text{C}}$ T + P $\xrightarrow{850^\circ\text{C}}$ M or poorly ordered H $\xrightarrow{900^\circ\text{C}}$ H (high content of HCl)
	B $\xrightarrow{900^\circ\text{C}}$ H; P $\xrightarrow{850^\circ\text{C}}$ H; N $\xrightarrow{900-1000^\circ\text{C}}$ H
	NbO ₂ $\xrightarrow{320^\circ\text{C}}$ TT $\xrightarrow{410^\circ\text{C}}$ T $\xrightarrow{817^\circ\text{C}}$ B $\xrightarrow{960^\circ\text{C}}$ H
	H $\xrightarrow{650^\circ\text{C}}$ B (Mixtures of B and H \rightarrow B, P _(NbOCl₃) = 5 atm and P _(Cl₂) = 3.1 atm)

*The existence of I-high is denied [8].

heating type shown in fig. 3. This apparatus can be used at 150 kb and 900°C for 1 h. When the apparatus was used at 200 kb, creep was observed.

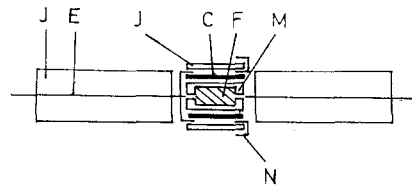


Figure 3

Figure 1 Diagram of the piston-cylinder apparatus.

Figure 2 Diagram of the "belt" apparatus.

Figure 3 Diagram of the Bridgman type apparatus.

A: Pb foil, B: talc, C: graphite, D: silica glass, E: thermocouple, F: sample, G: glass, H: cement, I: molten glass, J: pyrophyllite, K: nickel, L: steel, M: BN, N: gold foil.

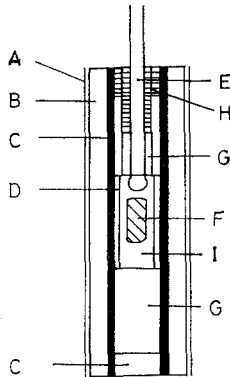


Figure 1

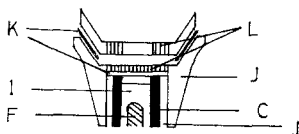


Figure 2

TABLE II Spectrographically standardised Nb₂O₅.

Fe	2 ppm
Mg	< 1 ppm
Ta	< 100 ppm
Ag, Al, As, Au, B, Ba, Be, Bi, Ca, Cd, Co, Cr, Cs, Cu, Ga, Ge, Hf, Hg, In, Ir, K, Li, Mn, Mo, Na, Ni, Os, P, Pb, Pd, Pt, Rb, Re, Rh, Ru, Sb, Se, Si, Sn, Sr, Te, Ti, Tl, V, W, Zn, Zr.	} undetectable

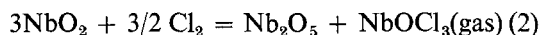
2.6. Procedure of Run

The samples were sealed in platinum or gold capsules to prevent reduction. The run was carried out by first applying the pressure, and then heating the sample for a given period. Each period was about 5 h. At the end of the run, it was quenched at a rate of approximately $100^\circ\text{C sec}^{-1}$ before the pressure was released. The volume of the sample for each run was about 30 mm^3 . Each sample after the run was analysed by X-ray diffraction, using a diffractometer with nickel-filtered copper radiation.

3. Results and Discussion

3.1. Distinct TT Form

The TT form was reported by Frevel and Rinn [4]. This form was produced as the first crystalline product (judging by X-ray diffraction) from "sulphate niobic acid" and "chloride niobic acid" on heating these at 500 to 600°C [5, 13, 18]. The amorphous niobic acid is converted into this form at about 440°C [5]. The TT form is also formed when NbO_2 is oxidised in air at 320 to 350°C , amorphous Nb_2O_5 being observed as intermediate [18]. In the reaction of NbO_2 with Cl_2 in accordance with the equation



at 270 to 320°C , the TT form was obtained [18]. This form was observed in the chemical transport of Nb_2O_5 in accordance with equation 1 for T_1 (low temperature side) = 350°C and T_2 (high temperature side) = 450°C [3, 18].

The results of the present work suggest that the distinct TT form is stabilised by means of trace impurities, as this form could be obtained only when less pure reagents were reacted in the vicinity of 800°C and 50 kb. The TT form has been indexed on the basis of a pseudohexagonal unit cell, $a' = 3.607\text{ \AA}$, $c' = 3.925\text{ \AA}$, (Frevel-Rinn), or $a' = 3.621\text{ \AA}$, $c' = 3.932\text{ \AA}$ (Terao). However, the present distinct TT form shows sharp X-ray diffraction patterns with splitting of the peaks so that it can be indexed on the basis of a monoclinic unit cell, $a = 7.23_8\text{ \AA}$, $b = 15.7_9\text{ \AA}$, $c = 7.18_8\text{ \AA}$, $\beta = 119^\circ 5_8$, $V = 711.7\text{ (\AA)}^3$ $z = 8$ molecules/cell.

The deviation from true hexagonality is associated with the difference between a and c , the value of β being very nearly equal to β for a hexagonal cell. Comparison with the results obtained by Frevel and Rinn [4] is made in table III. The following relations exist: $a \sim 2a'$, $b \sim 4c'$, $c \sim 2a'$, $V \sim 16V'$, $z \sim 16z'$. The primes refer to the results obtained by Frevel and Rinn.

TABLE III Comparison with the previously obtained X-ray diffraction results.

Distinct TT (present work)			TT (Frevel and Rinn [4])		
hkl	$d(\text{\AA})$	I	hkl	$d(\text{\AA})$	I
030	5.26 ₆	5			
040	3.94 ₈	100	001	3.925	90
200	3.13 ₆	90	100	3.124	100
002	3.11 ₃	45			
240	2.45 ₅	30	101	2.446	40
042	2.44 ₄	15			
080	1.97 ₄	30	002	1.962	30
402	1.81 ₀	15	110	1.800	25
202	1.80 ₄	20			
280	1.67 ₀	15	102	1.663	30
082	1.66 ₇	15			
442	1.64 ₅	10	111	1.637	14
242	1.64 ₁	10			
400	1.56 ₈	10	200	1.565	12
monoclinic cell			pseudohexagonal cell		
$a = 7.23_8\text{ \AA}$			$a' = 3.607\text{ \AA}$		
$b = 15.7_9\text{ \AA}$			$c' = 3.925\text{ \AA}$		
$c = 7.18_8\text{ \AA}$					
$\beta = 119^\circ 5_8$					
$V = 711.7\text{ (\AA)}^3$			$V = 44.22\text{ (\AA)}^3$		
$Z = 8$ molecules/cell			$Z = 0.5$ molecule/cell		

3.2. Direct Transitions from H to T and H to B

The transitions from T to H and from B to H under atmospheric pressure have been observed by previous workers. However, the direct reverse transitions have not been reported. The present study revealed that the reverse transitions are possible under high pressures. The T form has been considered as the low-temperature form. It is clear from the present experiment that the temperature range over which the T form is stable is extended considerably under high pressures. The results are shown in fig. 4 and summarised in table IV. The values of packing parameters $\lambda = V\rho/A$, where V = volume of ions, ρ = density, A = molecular weight, are, $\lambda = 0.49$ (H form), $\lambda = 0.54$ (T form), $\lambda = 0.57$ (B form).

From the Eyring theory the reaction-rate coefficient is given by:

$$k \propto \exp(-\Delta H^*/RT) \exp(\Delta S^*/R)$$

$$k_{(p)}/k_{(1)} = \exp\{(\Delta H_1^* - \Delta H_p^*)/RT\} \exp\{(\Delta S_p^* - \Delta S_1^*)/R\}$$

where $K_{(p)}$ is the reaction rate coefficient under pressure, ΔH^* is the activated enthalpy and ΔS^* the activated entropy. The value of $k_{(p)}/k_{(1)}$ may be increased by the effects of pressure and stress.

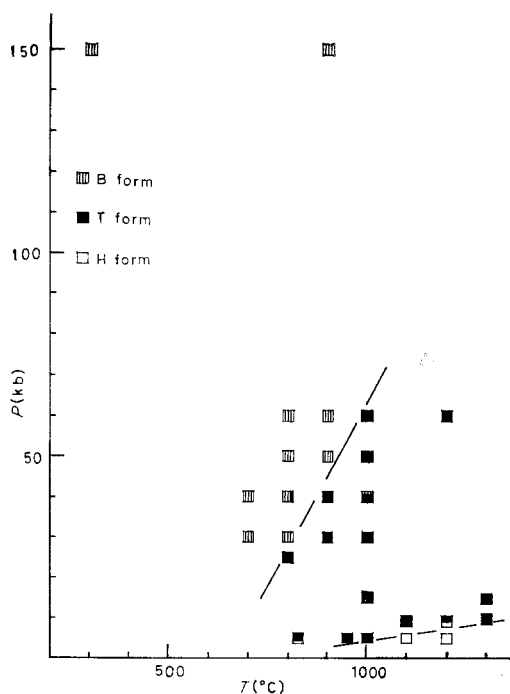


Figure 4 Pressure/temperature/structure relationships for Nb₂O₅.

TABLE IV Phase relations for Nb₂O₅.

H-T	T-B
$\Delta V = -5.1 \text{ cm}^3/\text{mol}$ at 1 atm.	$\Delta V = -3.1 \text{ cm}^3/\text{mol}$ at 1 atm.
$P_{(kb)} = 0.02T(^{\circ}\text{C}) - 15$	$P_{(kb)} = 0.18T(^{\circ}\text{C}) - 120$
$\Delta H \sim -3 \text{ kcal/mol}$ (exothermic)	$\Delta H \sim -10 \text{ kcal/mol}$ (exothermic)
$\Delta S \sim -2 \text{ cal/mol deg}$	$\Delta S \sim -10 \text{ cal/mol deg}$

When the H form was pressed at 150 kb and 300°C for several seconds, the B form obtained showed interesting X-ray patterns. The reflections from (1 $\bar{1}$ 1) and (111) were sharp, while the reflections from (400), (3 $\bar{1}$ 1) and (020), were diffuse. This may indicate that the arrangements of (1 $\bar{1}$ 1) and (111) planes are completed before the arrangements of (400), (3 $\bar{1}$ 1) and (020) planes, and this may be understood better when the structure of the B form is looked into.

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