

The Modifications of Niobium Pentoxide^[1]

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Dedicated with sincere good wishes to Professor Wilhelm Klemm on his 70th birthday

Niobium pentoxide crystallizes in numerous modifications. The present paper describes their mode of formation, structures, and thermal properties.

1. Introduction

In his fundamental work on the oxides of niobium^[2], Brauer distinguished three modifications of niobium pentoxide which, according to their appearance at low, medium, and high temperatures, are denoted by the letters T, M, and H. In the last few years other modifications have been found, and numerous observations have been made on the modes of formation, the structural principles, and the stabilities of these materials. The abundance of observations makes it desirable to subject the available material to a critical review and classification, and thus simultaneously to create a basis for further investigations.

2. What is a "Modification"?

The classical concept of polymorphism and its definition of modifications appears unambiguous when we think of, for example, sulfur or phosphorus, but its clarity diminishes when closely related structures are present between which transitions are possible. In such cases a discussion of whether particular modifications exist is not of fundamental importance, since it would be sufficient to characterize the materials by an accurate description of their structure. However, such characterization is still not possible for many substances, and the convenient concept of polymorphism will be abandoned only with reluctance. We must therefore attempt to obtain a more precise definition.

As an example, consider a material MX which – like ZnS – can be prepared in a cubic sequence ABC ABC ABC... and also in a hexagonal sequence AB, AB, AB.... It is then correct to speak of cubic and hexagonal modifications. Assume now that it is possible to link these two modifications in some way through a region of homogeneity with a statistical distribution of ABC and AB sequences. Even then it appears meaningful to speak of the limiting forms with purely cubic or purely hexagonal structure as modifications, although

thermodynamically they belong to the same phase. Obviously, however, it is no longer meaningful to regard any particular compositions $(ABC)_x(AB)_y$ within the range of homogeneity as modifications. However, a regular sequence such as ABC AB ABC AB... must be described as another modification. In this sense, a modification merely requires an ordered structure: *a corresponding ideal structure can be given for a modification*. It is immaterial for this definition that the actual crystal possesses structure defects. It is equally immaterial whether homogeneity regions or considerable concentrations of vacancies occur (in unordered distribution).

It should be particularly noted that the frequently coincident terms "modification" and "thermodynamic phase" are independent of one another. The definition does not exclude the possibility that – as discussed – several modifications may occur in one phase, or several phases may belong to the same modification. Obviously, however, this will not usually occur.

The above indicates how the concept of modification is to be understood in what follows. Frequently, the structurally less definite symbolism Nb₂O₅ in the X-form, e.g. in the M-form (or M-Nb₂O₅) is to be preferred because of insufficient knowledge of the structure.

3. Designation and Characterization of the Modifications (Forms) of Niobium Pentoxide

If all the phases (or modifications) occurring in a chemical system are known, it is convenient to denote these by a sequence of letters $\alpha, \beta, \gamma, \dots$ which simultaneously gives a sequence in stability or in composition. Such knowledge is still lacking in the case of niobium pentoxide, and for this reason nomenclature proposals of this type are premature and confusing (Table 1). We prefer the neutral symbols given in the first column of Table 1. In almost all cases, these were used also by the authors who first observed the corresponding modification.

The form Nb₂O₅-II observed by Shafer and Roy^[3] and identified with Brauer's M-Nb₂O₅^[2] is mentioned with the M-form. However, Nb₂O₅-II is, according to the interplanar

[1] 49th Communication on "Contributions to the Chemistry of Niobium and Tantalum". 48th Communication: H. Schäfer and D. Bauer, Z. anorg. allg. Chem., in press.

[2] G. Brauer, Z. anorg. allg. Chem. 248, 1 (1941).

[3] M. W. Shafer and R. Roy, Z. Kristallogr., Kristallgeometr., Kristallphysik, Kristallchem. 110, 241 (1958).

Table 1. Designations of the forms of Nb₂O₅. The authors mentioned at the head of each column use the symbols given in that column.

This paper (derivation)	Brauer [2]	Frevel and Rinn [5]	Holtzberg et al. [4, 6] Laves [7, 8] Zvinchuk [9]	Terao [10, 11]	Gold- schmidt [12]	Nowotny [13]	Shafer and Roy [3]	Schäfer et al.
TT(tief-tief) (low-low)		pseudo- hexagonal modific.[5]	δ [6] (γ' [6])	δ		diffuse α-form		TT [14, 15]
T (tief) (low)	T [2]		γ [6]	γ	α [12]	α	III [3]	
B (Blätter) (plates)			ζ [7]	γ' [11]				B [15]
M (medium)	M [2]		β [6] (α' [6])	β	precursor of β	β	II [3]	
H (high)			α [6]	α	β [12]	β' [13]	I [3]	
N (needles)	H [2]		τ, [8]					N [15, 16]
P (prisms)			ε [4]					P [15]
ε								
I-high							I-high [3]	
II							II [3]	
ox I to ox VI (oxidation)								ox I to ox VI [18]

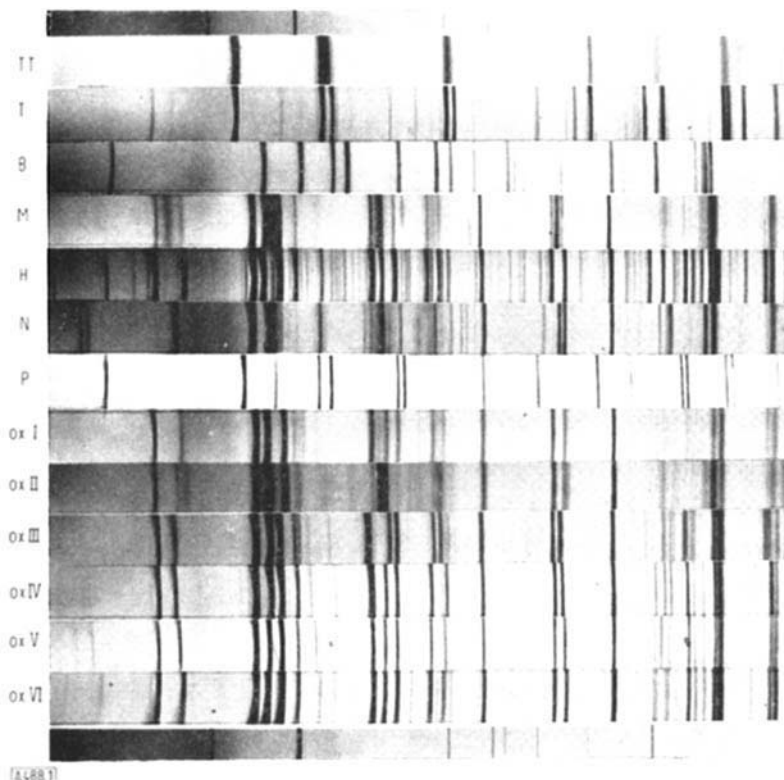


Fig. 1. Guinier photographs of the Nb₂O₅-forms TT, T, B, M, H, N, P, and oxI to oxVI. Cu-Kα₁ radiation. Top and bottom: α-quartz for comparison. Range of angles: Θ = 5 to 30°.

spacings reported^[3], different from all known forms of niobium pentoxide^[4] and has therefore also been cited as a new phase.

In the X-ray characterization of Nb₂O₅ samples, the large number of lines in the powder diagram and the often slight difference between the X-ray patterns of

related modifications must be borne in mind. Guinier photographs with Cu-Kα₁ radiation are particularly suitable because of the high resolution possible (Fig. 1). The X-ray patterns of the T-, B-, M-, N-, and P-forms are derived from samples prepared by chemical transport (cf. Section 4) in crystals of millimeter size. Interplanar spacings (d values) for most of the observed forms of Nb₂O₅ are given in the literature (Table 2). The table also indicates those literature data which agree particularly well with our own observations. Numerical values will therefore be given below only for the M-form.

[4] A. Reisman and F. Holtzberg, J. Amer. chem. Soc. 81, 3182 (1959).

[5] L. K. Frevel and H. W. Rinn, Analytic. Chem. 27, 1329 (1955).

[6] F. Holtzberg, A. Reisman, M. Berry, and M. Berkenblit, J. Amer. chem. Soc. 79, 2039 (1957).

[7] F. Laves, R. Moser, and W. Petter, Naturwissenschaften 51, 356 (1964).

[8] F. Laves, W. Petter, and H. Wulf, Naturwissenschaften 51, 633 (1964).

[9] R. A. Zvinchuk, Soviet Physics Crystallogr. 3, 750 (1959).

[10] N. Terao, Japan. J. appl. Physics 2, 156 (1963).

[11] N. Terao, Japan. J. appl. Physics 4, 8 (1965).

[12] H. J. Goldschmidt, J. Inst. Metals 87, 235 (1958/59).

[13] H. Nowotny, F. Benesovsky, E. Rudy, and A. Wittmann, Mh. Chem. 91, 975 (1960).

[14] F. Schulte, Thesis, Universität Münster, 1962.

[15] H. Schäfer, F. Schulte, and R. Gruehn, Angew. Chem. 76, 536 (1964); Angew. Chem. internat. Edit. 3, 511 (1964).

[16] This notation is also used by Andersson [17].

[17] S. Andersson, International Conference on Electron Diffraction and Crystal Defects, Melbourne 1965, II D-2.

[18] R. Gruehn and D. Bergner, unpublished work.

The selection of an X-ray pattern of the M-form suitable as a "standard" for this form presents difficulties: some preparations [25–27] have given Guinier photographs differing clearly from *Brauer's* M–Nb₂O₅ diagram [2]. Other data [9, 11, 22] differ from those of *Brauer* [2] and also to some extent from our own values. In order to be able to describe the X-ray pattern of the M-form, taking into account its variability [11, 13] (which we have also observed), it is convenient to distinguish between two groups of reflections (Table 3):

1. Diffuse reflections with *d* values (e.g. 4.88, 3.57, 2.05 Å) for which no lines of the H-form exist. These diffuse reflections disappear in the M → H conversion by a decrease in their intensity without any observed splitting.

2. Some sharp and some diffuse reflections, whose lines can be assigned to H–Nb₂O₅ with the same or almost the same value of *d*.

Brauer's M–Nb₂O₅ diagram [2] contains all the lines of group 1 and also all the diffuse and some sharp reflections of group 2; Guinier photographs of our preparations, however, show other sharp reflections of group 2, which we have denoted in Table 3 by 2+. If the different resolving power of the Guinier compared with the Debye method is taken into account, it would be conceivable that the additional reflections (2+) were unobservable on Debye photographs [2]. However, we cannot exclude the possibility that these reflections arise from a partial M → H–Nb₂O₅ conversion and therefore cannot be ascribed to pure M–Nb₂O₅. Since, however, our preparations, which were obtained in various ways (cf. Section 4) as powders or needle-like crystals, all give the (2+) reflections, we consider it likely that sufficiently ordered M–Nb₂O₅ preparations give all the

Table 3. Interplanar spacings (*d*) and estimated intensities (*I*) of the M-form of Nb₂O₅. The diffuse reflections (*I* in parentheses) are decisive for the detection of M–Nb₂O₅.

<i>d</i> [Å]	<i>I</i>	Group (cf. text)	<i>d</i> [Å]	<i>I</i>	Group (cf. text)
5.12	2	2	2.54	5	2
4.88	(1)	1	2.49	4	2+
4.63	2	2	2.31	6	2
3.86	1	2	2.07	3	2+
3.75	10	2	2.05	(4)	1
3.64	6	2	2.04	3	2+
3.57	(8)	1	1.91	8	2
3.49	6	2	1.78	(3)	2
3.36	3	2	1.70	1	2
3.16	1	2	1.69	4	2+
2.83	5	2	1.68	(5)	2
2.77	(6)	2	1.67	4	2+
2.70	3	2			

reflections mentioned (Table 3) [28]. The ratio of the intensities of the diffuse and the sharp reflections depends on the degree of order of the preparations; variations in the literature data are thus understandable.

Table 2. List of references on interplanar spacings (*d* or Θ values) and on intensities of X-ray reflections. The references in braces give results which are in best agreement with our own observations. The references in parentheses do not give *d* values but, for example, line diagrams.

TT	{[5]}	{[6, 13]}	{[10]}
T [19]	{[12]}	{[6, 13, 22]}	[2, 5, 10, 20, 21, 23]
B	{[7, 15]}		[11]
M		{[22]}	[2, 9, 11]
H	{[10, 12, 24]}	{[22]}	[2, 6, 9, 21]
N	{[15]}		
P	{[15]}		
I-high			[3] Not repeated by
II			[3] the present authors
oxI-oxVI	Not yet published [18].		

[19] The data of *R. B. Hahn* [20] have been ascribed by *Nowotny et al.* [13] to the TT-form.

[20] *R. B. Hahn*, *J. Amer. chem. Soc.* 73, 5091 (1951).

[21] *H. Inouye*, U.S. Atomic Energy Commission Publ. 1953 (ORNL-156).

[22] *H. Schäfer*, *A. Dürkop*, and *M. Jori*, *Z. anorg. allg. Chem.* 275, 289 (1954).

[23] *D. W. Bridges* and *W. M. Fassell*, *J. electrochem. Soc.* 103, 326 (1956).

[24] *A. Magnéli* and *S. Lagergren*, A.S.T.M. Index-Card 5-0379/80. These lattice constants, however, are incorrect (personal communication from *R. Norin*). Correct data: *a* = 21.23 Å; *b* = 3.824 Å; *c* = 19.43 Å; β = 120° 10'; cf. [52].

[25] *H. Schäfer*, *R. Gruhn*, and *M. Hiesker*, unpublished work.

[26] *H. Schäfer*, *R. Gruhn*, and *M. Rönspiess*, unpublished work.

[27] *R. Gruhn* and *M. Görbing*, unpublished work.

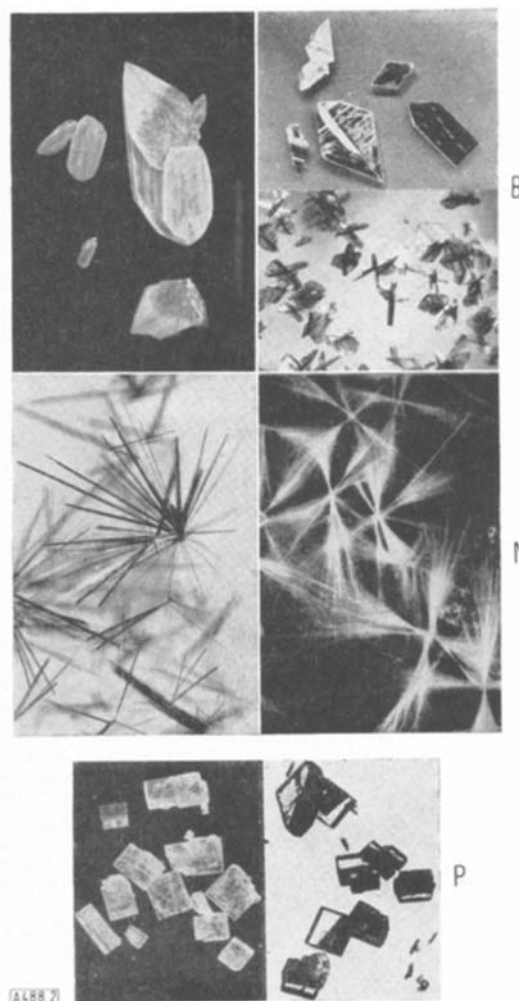


Fig. 2. Crystals of the T-, B-, H-, N-, and P-forms of Nb₂O₅. The lengths of the needle-shaped crystals shown (H, N) are 4 to 8 mm, the size of the prisms (P) is 1 to 2 mm, while T- and B–Nb₂O₅ form 5 to 10 mm single crystals. The crystals of the T-form are optically turbid but behave as single crystals to X-rays.

[28] Single-crystal investigations on this subject are in progress (*W. Mertin*, Münster).

[29] Calculated by us from the lattice constants [5].

[30] For these measurements we are obliged to Miss *M. Rönspiess*.

Table 4 gives lattice constants, X-ray densities, and molar volumes calculated from these data, together with pycnometrically determined densities. In addition, the following densities have been measured pycnometrically: amorphous Nb₂O₅ obtained from "chloride niobic acid": 4.36 g/cm³ [6], amorphous Nb₂O₅ (from NbO₂): 5.12 g/cm³ [41]; N-Nb₂O₅: 4.59 g/cm³ [30]; P-Nb₂O₅: 4.50 g/cm³ [30].

Fig. 2 shows crystal photographs of the T-, B-, H-, N-, and P-forms of Nb₂O₅. The crystals were prepared by the chemical transport of Nb₂O₅ (see below). An illustration of the M-form is not given, since it crystallizes in needles like the H-form.

is obtained, for example by oxidation, the resulting form may depend on the nature of the starting material. Moreover, small amounts of impurities may have a stabilizing or directing effect. If the starting material used is "niobic acid" separated from aqueous solution, then in addition to the presence of water, the presence of foreign ions is also of importance. In this connection, we call the niobic acid precipitated from a pyrosulfate digestion "sulfate niobic acid". These preparations of "sulfate niobic acid" (or "chloride niobic acid", etc.) are carefully washed and have only a small (but detectable) content of sulfate (or chloride, etc.), which cannot be reduced by further washing.

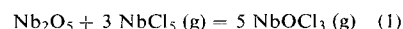
Table 4. Lattice parameters and densities of some forms of Nb₂O₅.

Form of Nb ₂ O ₅	Lattice constants [Å]	Space group or crystal system	Formula units Nb ₂ O ₅ /cell	Density [g/cm ³]		Molar volume [cm ³] M(Nb ₂ O ₅) (from DX-ray)	References and Remarks
				DX-ray	D _{pyk}		
TT	a = 3.607; c = 3.925	"pseudo-hexagonal"	0.5	4.99 [29]	—	53.3	[5] similar data for "hexag." unit cell in [10]
T	—	—	—	—	4.86	—	[30]
	a = 6.19; b = 3.65; c = 3.94	orthorhombic	—	—	—	—	[31]; similar data in [10, 32]
	a = 6.24; b = 43.79; c = 3.92	orthorhombic	12	4.94	—	53.8	[9]
	a = 7.31; b = 15.72; c = 10.75; β = 120°42'	monoclinic	12	4.99 [33]	—	53.3	[5]; similar data for monoclinic unit cell in [10]
B	—	—	—	—	5.17	—	[6]
	a = 12.73; b = 5.56; c = 4.88; γ = 105°05'	—	—	—	5.04	—	[30]
	a = 7.348; b = 5.962; c = 13.646; β = 115°30'	monoclinic	4	5.29	—	50.2	[8]; structure investigated on single crystals [11]
M	—	—	—	—	5.19	—	[14]
	a = 20.28; b = 3.83; c = 20.28; β = 120°	monoclinic	15	3.84	—	54.8	[9]
	a = 22.10; b = 7.638; c = 19.52; β = 118°15'	monoclinic	—	—	—	—	[11]
H	—	—	—	—	4.3–4.4	(62–60) [34]	[30]
	a = 21.50; b = 3.825; c = 20.60; β = 121°45'	monoclinic	14	4.29	—	—	[24]; lattice constants do not correspond to the indices given [6, 24a]
	a = 21.34; b = 3.816; c = 19.47; β = 120°20'	monoclinic	14	4.52	4.55	58.8	[6]; similar data in [10, 32]
	a = 19.63; b = 3.835; c = 20.93; β = 120°	monoclinic	14	4.53	4.46	58.7	[3]
	a = 20.39; b = 3.82; c = 19.47; β = 115°39'	monoclinic	14	4.51	—	58.9	[9]
	a = 21.16; b = 3.822; c = 19.35; β = 119°50'	P 2	14	4.55	4.55 [6]	58.4	[35]; structure investigated with single crystals
	—	—	—	—	—	—	—

4. Modes of Formation

Niobium pentoxide can be obtained in many different ways. If the solid oxide is heated for some time at temperatures above 1000 to 1200°C, the H-form, which is stable under these conditions, is always produced. The forms of Nb₂O₅ prepared at lower temperatures are mostly metastable (cf. Section 7). The method of preparation then also plays a decisive part. If the Nb₂O₅

The chemical transport [36] of niobium pentoxide is of particular importance; the reversible formation of gaseous oxide halides NbOX₃ (with X = Cl, Br, I) is utilized [37]. For the chloride system, used most frequently, we have



This transporting reaction is endothermic, so that Nb₂O₅ is consumed in the hot zone (T₂) of the reaction tube and deposited in the less hot zone (T₁) [37a]. The

[31] W. T. Holser, Acta crystallogr. 9, 196 (1956).

[32] O. Kubaschewski and B. E. Hopkins, J. less-common Metals 2, 172 (1960).

[33] Calculated [6] from the lattice constants [5].

[34] Calculated by us from the pycnometric density [30].

[35] B. M. Gatehouse and A. D. Wadsley, Acta crystallogr. 17, 1545 (1964).

[36] H. Schäfer: Chemische Transportreaktionen. Verlag Chemie, Weinheim 1962.

[37] H. Schäfer and M. Hüesker, Z. anorg. allg. Chem. 317, 321 (1962).

[37a] Under somewhat modified conditions, the transport can also take place exothermally, i.e. into the hotter zone, in accordance with the scheme $\text{Nb}_2\text{O}_5 + 3 \text{NbX}_4 (\text{g}) + 3 \text{Xg} = 5 \text{NbOX}_3 (\text{g})$.

This is important particularly in the preparation of NbOx phases (x < 2.5) [25].

transport is carried out in the presence of free chlorine [$p(\text{Cl}_2) = 1 \text{ atm}$, 20°C], so that the appearance of reduced NbO_x phases ($x < 2.50$) is suppressed. The procedure followed in the transport experiments will be described below using $\text{H-Nb}_2\text{O}_5$ as an example. Fig. 3 shows a transport tube before charging.

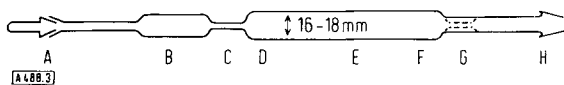


Fig. 3. Charging of a transport tube (fused silica). Length DEF: 12 to 13 cm.

A known amount of Nb_2O_5 (250–700 mg) is introduced into the reaction tube at D from H, and subsequently a capillary is drawn at G. After part B of the tube has been charged with the calculated amount of Nb, and A has been closed, the tube is evacuated from H and the section of the tube C–G is heated with a bunsen flame. After cooling, a stream of purified Cl_2 is passed through the tube from A. When the air has been displaced, the Nb at B is ignited and NbCl_5 is condensed at DEF. The cooled tube, filled with Cl_2 at 1 atm (room temperature) is sealed off at C and G. The transport tube C–G has then been charged.

It is then introduced into the predetermined temperature gradient in a horizontal or, if desired, in a sloping position (convection) where it remains for from 3 to 8 days. Under these conditions, the transport of Nb_2O_5 from T_2 to T_1 takes place with the aid of the reversible establishment of the equilibrium (1). If heating is to be discontinued, first only Section D of the tube is removed from the oven, so that the contents of the gas phase deposit there and do not contaminate the transported crystals that have already deposited at EF.

Fig. 4 shows a transport tube with $\text{H-Nb}_2\text{O}_5$ crystals. The white substance on the left-hand side of the tube consists of the condensed contents of the gas phase (essentially NbOCl_3).

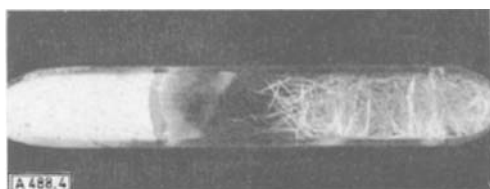


Fig. 4. Transport tube with crystals of $\text{H-Nb}_2\text{O}_5$. Left: NbOCl_3 condensate.

The occurrence of oxygen-poorer NbO_x phases, which is observed, for example, during chemical transport in the absence of Cl_2 , has also been studied [26, 37–39]. It is important in connection with the forms of Nb_2O_5 oxI to oxVI, and it may be mentioned that the O:Nb ratio can be obtained very accurately *via* determination of the Nb^{4+} content.

For a direct determination of small contents of Nb^{4+} [40], samples of 3–15 mg are introduced under vacuum into a degassed KOH-KBr melt, whereupon all the substance dissolves in the form of niobate(V) and an amount of hydrogen equivalent to the content of Nb^{4+} is liberated. The gas evolved is pumped off, compressed with a Töpler pump, and its volume measured in a mercury gas buret; it can also be

[38] R. Gruhn and H. Schäfer, *Naturwissenschaften* 50, 642 (1963).

[39] R. Gruhn, D. Bergner, and H. Schäfer, Lecture, Clausthal 1965. Summary: *Angew. Chem.* 77, 1082 (1965); *Angew. Chem. internat. Edit.* 4, 1087 (1965).

[40] R. Gruhn, unpublished work.

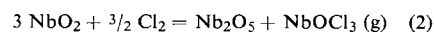
identified by combustion over CuO . The limits of error may be characterized by the analytical compositions $\text{NbO}_{2.420} \pm 0.004$ and $\text{NbO}_{2.480} \pm 0.001$.

Preparations of all modifications investigated so far with the composition $\text{NbO}_{2.49}$ already have a definite blue color. An oxygen deficiency cannot, therefore, be made responsible for the occurrence of numerous colorless forms of Nb_2O_5 . Contrary assumptions [11, 13] are incorrect.

TT- Nb_2O_5

This form, first described by Frevel and Rinn [5], was produced as the first state crystalline to X-rays [6] from “sulfate niobic acid” and “chloride niobic acid” on heating at 500 to 600°C [3, 6, 14]; with longer times of heating, amorphous niobic acid is converted into TT- Nb_2O_5 at even lower temperature (*e.g.* 440°C [6]) [41]. Different samples of niobic acid prepared in the same way may exhibit different rates of conversion, so that an X-ray check is always necessary.

The TT-oxide is also formed when NbO_2 is oxidized in air at 320 to 350°C [41a], amorphous Nb_2O_5 being observed as an intermediate [41]. If the oxidation is carried out at higher temperatures (350 to 500°C), TT- Nb_2O_5 is obtained only with very short reaction times [41]. In the reaction of NbO_2 with Cl_2 , in accordance with the equation



at 270 to 320°C , we again obtained the TT-form [41]. The TT-form can also be obtained by oxidation of niobium alloys in air at, for instance, 800°C [13], as well as by the slow oxidation of Nb or lower oxides arising from it under special conditions [10]. Moreover, TT- Nb_2O_5 (together with $\text{Nb}_3\text{O}_7\text{Cl}$) has been observed in the chemical transport of Nb_2O_5 in accordance with Eq. (1) for $T_1 = 350^\circ\text{C}$ and $T_2 = 450^\circ\text{C}$ [15, 26].

The 24-hour oxidation of Nb_2O_5 with air at 320°C is to be recommended as a method of preparing pure TT- Nb_2O_5 .

T- Nb_2O_5

This form, described by Brauer [2], appears when “sulfate niobic acid” or “chloride niobic acid” is heated at 600 to 800°C [3, 6, 41]. Prolonged heating at, for example, 400°C (3 days) also leads to the T form [41]. In addition, it can be obtained from TT- Nb_2O_5 , which changes almost continuously into T- Nb_2O_5 on being heated at 600 to 800°C [41]. The T-form arises in a short time already at temperatures over 400°C from TT- Nb_2O_5 obtained by the oxidation of NbO_2 in air at 320 to 350°C [41]. If NbO_2 is oxidized in air at 600 to 800°C , T- Nb_2O_5 is produced after a short time [41]. It is also produced in the oxidation of Nb or Nb alloys below 1000°C [13]. Under hydrothermal conditions ($P = 170 \text{ atm}$, $T = 330\text{--}380^\circ\text{C}$), amorphous “niobic acid”

[41] C. Brendel, Münster, unpublished work.

[41a] TT- Nb_2O_5 produced in this way may still contain some amorphous Nb_2O_5 .

also changes into T-Nb₂O₅ [3]. We have now obtained the T-form in single crystals by quenching supercooled Nb₂O₅ melts [42] and also by the chemical transport of Nb₂O₅ in accordance with Eq. (1) [26, 43].

For crystal formation by means of chemical transport a device has proved satisfactory which permits nucleation and crystal growth to be observed visually at the experimental temperature. A "fused silica oven" constructed for this purpose simultaneously permits a favorable rate of nucleation to be established by varying T₂-T₁ at constant T₁.

In principle, the following arrangement has been used [43]: a fused silica transport tube is fixed centrally in a horizontal silica tube of correspondingly larger cross-section, which carries the two heating coils for establishing the temperatures T₁ and T₂. The outer cladding of this oven has openings which permit nucleation and the growth of crystals to be observed between the windings of the heating coil. For example, for the preparation of T-Nb₂O₅, the temperature is first controlled such that T₂ = 890 °C and T₁ = 835 °C. Under these conditions, nuclei of T-Nb₂O₅ (and of B- and N-Nb₂O₅) can be formed. If it can be seen from the shape of the crystals (and from the color, which is yellowish at high temperatures for all Nb₂O₅ modifications except B-Nb₂O₅) that only T-Nb₂O₅ has been produced at T₁, T₂-T₁ is reduced by lowering T₂ to 875 °C. This prevents the formation of new nuclei, while the crystals which are already present grow further. The subsequent time of transport is, for example, 5 days. If unwanted crystals of other forms are formed, all nuclei can be removed again by interchanging T₁ and T₂.

The following procedures are recommended for the preparation of T-Nb₂O₅ powder:

1. Dehydration of substantially chloride-free washed "chloride niobic acid" at 400 °C (2 hours) with subsequent heating to 600 to 800 °C (10 hours).
2. Oxidation of NbO₂ in air at 400 °C for 4 to 5 hours. Samples of T-Nb₂O₅ prepared by methods 1 and 2, which cannot be distinguished by their Guinier diagrams, nevertheless show different transformation behavior on further heating [41] (cf. Section 5).

B-Nb₂O₅

This form was first observed in the chemical transport of Nb₂O₅ in accordance with Eq. (1) when the deposition temperature T₁ was 750 to 850 °C and T₂-T₁ 100 °C [14, 15] (cf. also [7]). Under these conditions, N-Nb₂O₅ and P-Nb₂O₅ are formed in addition to B-Nb₂O₅, but the characteristic plate-like crystals of the B-form can easily be sorted out. Fig. 5 shows crystals of B- and N-Nb₂O₅ that have deposited together in the transport tube. Growth of large untwinned single crystals (cf. Fig. 2) can be achieved in the fused silica oven in the manner described for T-Nb₂O₅. Here again, by selection of nuclei, it is possible to obtain B-Nb₂O₅ alone, without contamination by other forms of Nb₂O₅ [43].

If Nb₂O₅ is transported in accordance with Eq. (1) (or by means of the analogous bromide or iodide systems), all the forms of Nb₂O₅ obtainable in this way (T, M, H,

N, P, B) can be obtained with a blue color, *i.e.* with a low content of Nb⁴⁺ [25, 26]. However, colorless crystals of stoichiometric composition are obtained when the transport according to Eq. (1) is carried out in an oxidizing atmosphere produced by the introduction of chlorine into the transport tube [P(Cl₂) = 1 atm, 20 °C]. Even under these conditions, however, the B-form – and only



Fig. 5. Transport tube with crystals of B- and N-Nb₂O₅ deposited together.

this – is usually produced with light blue color [15] (composition, for example, Nb₂O_{4.994}). This color further facilitates hand-sorting of crystals of the B-form from mixtures; at higher temperatures it changes to pale green.

The Nb⁴⁺ content of the blue B-crystals was hardly lowered on ignition (800 °C) in air for several hours [44]. After 80 hours, however, appreciable decoloration had occurred, and after 800 hours the crystals became practically colorless [40].

Crystals of B-Nb₂O₅ obtained by the transport method contained less than 0.01 % of Cl [44]. However, this Cl content is not characteristic of the B-modification, since the latter can also be obtained free from chlorine by the oxidation of NbO₂.

During transport in the temperature gradient, the nature of the Nb₂O₅ added at T₂ does not affect the form of Nb₂O₅ depositing at T₁. Usually H-Nb₂O₅ was used as the starting material.

On prolonged isothermal heating at 750 °C in the presence of NbOCl₃ as transporting agent, we obtained [26] the pure B-form from T-Nb₂O₅ and P-Nb₂O₅ [45]. If H-nuclei are also present under these conditions, B-Nb₂O₅ is converted into the H-form already at 750 °C [26]; cf. Section 7.

TT-Nb₂O₅ and T-Nb₂O₅ prepared by the oxidation of NbO₂ in air are converted into the B-form [11, 41] by further heating in air (*e.g.* for a few hours at 800 °C; 180 hours at 500 °C) [41]. It is also possible, although less convenient, to start from metallic Nb.

The oxidation of NbO₂ in air (24 hours at 320 °C and 24 hours at 850 °C for the subsequent TT → T → B conversion) may be recommended for the preparation of pure B-Nb₂O₅ powder.

[44] R. Gruehn, F. Schulte, and H. Schäfer, *Angew. Chem.* 76, 685 (1964); *Angew. Chem. internat. Edit.* 3, 634 (1964).

[45] All T-Nb₂O₅ preparations undergo this T → B conversion, regardless of their history.

M—Nb₂O₅

This form, first observed by *Brauer* [2], arises when "sulfate niobic acid" or "chloride niobic acid", or the T-form obtained from "sulfate" or "chloride" niobic acid is heated for some hours at 900 to 950 °C [14, 27] (or possibly a shorter time at a higher temperature [2, 6]). The M-form has also been observed in the oxidation of Nb and Nb alloys at 1000 °C in air [13] and in the chemical transport of Nb₂O₅ via NbOCl₃ or NbOBr₃, with T₁ = 850 to 900 °C and T₂–T₁ = 100 °C [14, 25, 26].

It is difficult to prepare pure M-Nb₂O₅, since considerable amounts of H-Nb₂O₅ are frequently produced together with the M-form (cf. Section 3). In transport experiments, moreover, M-Nb₂O₅ and N-Nb₂O₅ may be deposited together. There is as yet no reliable method of preparation of the pure M-form.

H—Nb₂O₅

This modification of niobium pentoxide is particularly easy to obtain. As far as is known, H-Nb₂O₅ arises from any other form on heating in air to about 1100 °C. The same result is obtained when precipitates of niobic acid, *e.g.* from solutions containing sulfate, chloride, bromide, iodide, or fluoride, are heated at 1100 °C or when metallic niobium or lower oxides (NbO, NbO₂, NbO_x) are oxidized in air at this temperature to Nb₂O₅. If single crystals of the M-form are heated at 1100 °C, the single-crystal nature is retained in the transformation to the H-form, while crystals of all other forms of Nb₂O₅ are converted into polycrystalline H-Nb₂O₅ [44].

The H-form is also produced under hydrothermal conditions (P = 170 atm, T = 1075 °C) [3] and from a melt when, to avoid separation of T-Nb₂O₅, it is seeded with H-Nb₂O₅ or is cooled very slowly [42] (cf. also [4]). By chemical transport in accordance with Eq. (1), the pure H-form deposits [14] when the lower temperature T₁ of the transport tube is at least 950 °C [26]; cf. Fig. 4. In the presence of H-nuclei (cf. B-Nb₂O₅) or in the presence of HCl as transporting agent [P(HCl) = 1 atm, 20 °C] we obtained H-Nb₂O₅ even at 750 °C [26].

N—Nb₂O₅

This form arose first in the chemical transport of Nb₂O₅ [14, 15] in accordance with Eq. (1), the temperature of separation T₁ being 830 to 840 °C and T₂–T₁ 90 to 100 °C [26]. Under these conditions, often mixtures of N- with M- or H-Nb₂O₅ and also some B-Nb₂O₅ were obtained. The bundles of needles of N-Nb₂O₅ (Figs. 2 and 5) can, however, easily be distinguished.

The formation of the N-form is promoted by the presence of small amounts of fluoride [17, 26]. Thus by chemical transport we obtained only the N-form when the quartz tube had been cleaned with dilute hydrofluoric acid (subsequently rinsed with water and heated in vacuum) or when the transport tube contained a little fluoride, *e.g.* 5 mg of NbO₂F per 500 mg Nb₂O₅, in addition to the other materials. The N-Nb₂O₅ obtained in this way contained < 0.1 % of F [26, 46]. However, even

[46] In the presence of fluorides, SiO₂ can be transported from the quartz wall onto the deposited N-Nb₂O₅ crystals; the amorphous SiO₂ adhering to the surface simulates a high SiO₂-content [15] of the Nb₂O₅ [27].

when F was rigorously excluded, crystals of the N-form could be produced by chemical transport, particularly by the selection of nuclei in the fused silica oven (T₁ = 840 °C; T₂ = 900 °C; cf. T-Nb₂O₅) [43]. The N-form has also been obtained under hydrothermal conditions (2000 atm, 900 °C) [17], where OH probably plays the role of F.

Andersson and *Åström* [47] obtained N-Nb₂O₅ by thermal decomposition of NbO₂F; N-Nb₂O₅ obtained in this way contains about 0.2 % of F [48]. This method of preparation has been confirmed in our laboratory [49].

The order of magnitude of the F content of preparations of Nb₂O₅ has been determined by mass spectrometry. The samples were heated in a graphite crucible to incipient decomposition, and the ion currents corresponding to the gaseous fluorides produced were measured and integrated over time [48]. The limit of detection was 0.05 to 0.1 % of F. The compound Nb₃₁O₇₇F [17, 50] was used as an F standard. The mass-spectrometric determination therefore is based on the F-content proposed by structural analysis.

Thermal decomposition of NbO₂F can be recommended for the preparation of pulverulent N-Nb₂O₅ (containing about 0.2 % of F): NbO₂F is heated for some hours at 1000 °C in a high vacuum (with the pump running) [49]. Different preparations of NbO₂F can behave somewhat differently with respect to the decomposition temperature (see under P-Nb₂O₅). The course of the decomposition should be checked by X-ray analysis, since Nb₃O₇F [47, 70] may arise when the time of heating is too short and H-Nb₂O₅ when it is too long.

P—Nb₂O₅

This form first arose in the chemical transport of Nb₂O₅ in the chloride system [Eq. (1)], with T₁ = 750 °C and T₂–T₁ = 100 °C [14, 15]. Meanwhile it has also been prepared by the transport method by *Laves et al.* [8]. Analogous transport in the bromide and iodide systems also gives the P-form in admixture with T- and B-Nb₂O₅ at T₁ = 650 to 750 °C [25]. The experimental conditions and the specific formation of nuclei play a decisive part. This goes so far that in an earlier stage of the investigations [14] we thought that the P-form was thermodynamically stable over a certain range of temperatures and was obtainable from all other modifications. However, this view was not confirmed, and it is actually very difficult in some cases to obtain P-Nb₂O₅ by transport in the presence of NbOCl₃ and Cl₂.

New experiments have shown that the formation of P-Nb₂O₅ is promoted when the transport tube is filled, not with NbOCl₃ + Cl₂, but with Cl₂ (1 atm/20 °C) and small amounts of water, *e.g.* 0.04 to 0.12 mg of H₂O/ml of tube volume (T₁ = 600, T₂ = 800 °C). At present this appears to be the most satisfactory method for the preparation of P-Nb₂O₅ [26]. Possibly the formation of P-Nb₂O₅ observed previously in transport with NbOCl₃ + Cl₂ without the addition of water [14] should be ascribed to the water content of the silica.

[47] S. Andersson and A. Åström, Acta chem. scand., in press.

[48] K. Rinke, Münster; unpublished mass-spectrometric investigation.

[49] D. Giegling, Münster, unpublished work.

[50] We are obliged to Dr. S. Andersson for the sample.

We obtained the P-form in admixture with T-Nb₂O₅ by heating "chloride niobic acid" with a high content of HCl (e.g. 8%) to 650–800 °C (in air [15] or in a stream of moist HCl) [26]. The decomposition of Nb₃O₇Cl (in air or in vacuum) at 700 to 800 °C yielded corresponding polycrystalline mixtures of P-Nb₂O₅ and T-Nb₂O₅ [42].

The use of HCl-containing starting materials obviously has a promoting effect on the formation of P-Nb₂O₅. Nevertheless, analyses of P-Nb₂O₅ crystals obtained by chemical transport and of precipitates heated to 750 °C gave a Cl content of less than 0.01 % [14].

The P-form also arises during the very slow thermal decomposition (heating from room temperature to 740 °C over 5 days) [41] of NbO₂F, which can easily be obtained from Nb₂O₅ and hydrofluoric acid.

ε-Nb₂O₅

Reisman and *Holtzberg* [4] found a freezing point (1435 °C) corresponding to a metastable phase when an Nb₂O₅ melt was supercooled. The ε-Nb₂O₅ crystallizing under these conditions remained stable for a few hours above 1400 °C, but was converted exothermally into H-Nb₂O₅ on further cooling or on seeding with the latter material. Since it has so far been impossible to investigate this substance by X-rays, the possibility cannot be excluded that one of the known forms of Nb₂O₅ crystallized in a metastable state from the melt and caused the observed phenomenon.

Shafer and *Roy* considered their Nb₂O₅-II to be identical with *Brauer's* M-Nb₂O₅ [2], but the d values they give for Nb₂O₅-II can be assigned neither to the M-form nor to any other form of niobium pentoxide [4]. The behavior of Nb₂O₅ under hydrothermal conditions should be investigated further (cf. also the hydrothermal production of N-Nb₂O₅).

The oxI to oxVI Forms of Nb₂O₅ [18]

Closely similar NbO_x phases separated by heterogeneous regions [38, 39] can be prepared by chemical transport under reducing conditions [26] and by the reduction of Nb₂O₅ (or the oxidation of NbO₂) in an H₂/H₂O atmosphere, e.g. at 1300 °C [51]. Some of them have also been obtained by tempering oxide mixtures [52–54]. All these deep blue materials correspond to definite structures (Table 5) [35, 53–56]; there are two modifications of the compound NbO_{2.417}, corresponding to Nb₁₂O₂₉.

The oxidation of this material at 1100 °C in air leads to H-Nb₂O₅. A 4-hour oxidation at 650 °C, however, yields other colorless Nb₂O₅ preparations that we denote by oxI to oxVI. Their Guinier diagrams are related to those of the initial NbO_x phases, but differ from one another and from that of H-Nb₂O₅ (Fig. 1). On subsequent ignition (1100 °C), all these preparations change into the H-form.

Table 5. The Nb₂O₅ forms oxI to oxVI [18] and their origin.

Composition NbO _x by chemical analysis	NbO _{2.417} (I) [55a]	NbO _{2.417} (II) [55a]	NbO _{2.453} [55a]	NbO _{2.46} [39]	NbO _{2.467} to 2.480 [38, 39]	NbO _{2.483} [39]
Formula corr. to structural analysis	Nb ₁₂ O ₂₉ (I) [53, 55]	Nb ₁₂ O ₂₉ (II) [53]	Nb ₂₂ O ₅₄ [52, 55]		Nb ₂₅ O ₆₂ (upper limit of the phase) [54]	
Designation of the 650 °C oxidation product	oxI	oxII	oxIII	oxIV	oxV	oxVI

Nb₂O₅-I-high

This modification was described by *Shafer* and *Roy* [3] as a stable high-temperature form. According to differential thermal analysis and high-temperature X-ray photographs taken by these authors, at 1285 °C H-Nb₂O₅ is converted endothermally and reversibly into Nb₂O₅-I-high. The occurrence of this new stable form above 1250 °C has been queried by *Reisman* and *Holtzberg* [4], particularly since the d-values given for Nb₂O₅-I-high differ only slightly from those of H-Nb₂O₅. The substance observed [3] may have been an NbO_x phase with x < 2.5. More accurate investigations on this point should be carried out.

Nb₂O₅-II

This form was reported by *Shafer* and *Roy* [3], who obtained poorly crystalline Nb₂O₅-II by heating amorphous "niobic acid" to 880 to 950 °C in air; particularly well crystallized samples were obtained under hydrothermal conditions (P = 170 atm, T = 390 to 1060 °C).

The Nb₂O₅-forms oxI to oxVI are preparatively and X-radiographically defined. They are undoubtedly closely related. All (or some of them) might belong to the same mixed-crystal phase. Information on whether these materials are to be regarded as modifications in the sense of Section 2 can be given only by structural investigations.

Other Forms of Nb₂O₅

The multiplicity of the forms of Nb₂O₅ is not exhausted by those described above. At any rate, we possess some preparations of Nb₂O₅ with a different X-ray pattern, which have not yet been investigated further [26, 57].

[51] *D. Bergner*, Münster, unpublished work.

[52] *R. Norin* and *A. Magnéli*, *Naturwissenschaften* 47, 354 (1960).

[53] *R. Norin*, *Acta chem. scand.* 17, 1391 (1963).

[54] *R. Norin*, *Naturwissenschaften* 52, 300 (1965).

[55] *R. Norin*, personal communication.

[55a] For the assignments see *R. Gruhn* and *H. Schäfer*, *J. less-common Metals*, in press.

[56] *S. Andersson*, *Bull. Soc. chim. France* 1965, 1088.

[57] *L. Zylka*, Münster, unpublished work.

5. "Memory" of Solids

Niobium pentoxide provides a fine example of this term, introduced by Hüttig^[58]: $\text{T-Nb}_2\text{O}_5$ can be prepared in three ways; the resulting samples are not distinguishable by X-rays:

- By oxidation of NbO_2 (4–5 h in air) at 500 to 600 °C.
- By reaction of NbO_2 with Cl_2 ; 9–10 h, 270 to 300 °C; [cf. the formation of $\text{TT-Nb}_2\text{O}_5$ according to Eq. (2)]. Further heating (15 min at 500 °C in air).
- By heating "sulfate" or "chloride" niobic acid (2 h, 600 °C in air).

However, the preparations "remember" their different origins, and behave differently on further heating^[41]: Nb_2O_5 (a) is converted into $\text{B-Nb}_2\text{O}_5$ sharply at 817 °C (differential thermals analysis)

Nb_2O_5 (b) changes into $\text{B-Nb}_2\text{O}_5$ so slowly that the conversion is not complete even after 165 hours at 850 °C.

Nb_2O_5 (c) is converted into the forms $\text{M-Nb}_2\text{O}_5 + \text{H-Nb}_2\text{O}_5$ after heating for 16 hours at 800 °C. Here, therefore, the B-form has been passed over.

The basis of the "memory" of the three NbO_2 preparations has not yet been investigated. The first interpretation that comes to mind is incorporation of impurities or the presence of specific structural defects.

6. Structures

The crystal structures of the various forms of Nb_2O_5 are complicated. Accurate investigations of even the long-known forms have been undertaken only recently.

Octahedral elements are the decisive factor for the structure of the pentoxides. The stoichiometric O/Nb ratio of 2.5 can be achieved by the combination of various octahedral linkages, and this is the reason for the multiplicity of the Nb_2O_5 structures.

The situation is even more complicated, as in addition to crystal structures with all metal ions coordinated in a similar manner (a), there are also those containing cations of different coordination (type b; e.g. octahedral and tetrahedral coordination occur together). Type (a) includes a structure in which all the cations are surrounded octahedrally by O^{2-} particles. Under these conditions, in addition to a structure of similarly linked octahedra (e.g. the ReO_3 lattice), modifications are conceivable in which several types of O^{2-} octahedra can be distinguished by the distinct natures of their linkage in the lattice. The various ways of linking the O^{2-} octahedra are expressed formally by the extent to which the O^{2-} ions belonging to an octahedron must be ascribed to the corresponding cation^[59]. In this way, for example, the O^{2-} octahedra from which a hypothetical M_3O_8 structure^[60] could be constructed are divided into

two types: (1) octahedra which are joined by corners to all surrounding octahedra, so that each O^{2-} is to be reckoned as belonging to two octahedra. This type of linkage, which is present in ReO_3 , is designated $[\text{MO}_{6/2}]$ or $\text{MO}_{3.0}$. In addition, (2) octahedra joined by three corners (3 O^{2-}) and two edges (3 O^{2-} ; here with two other octahedra in each case), are necessary. They are symbolized by $[\text{MO}_{3/2} \text{O}_{3/3}]$ or $\text{MO}_{2.50}$ (cf. Fig. 6). $\text{MO}_{3.0} + 2 \text{MO}_{2.50}$ give M_3O_8 .

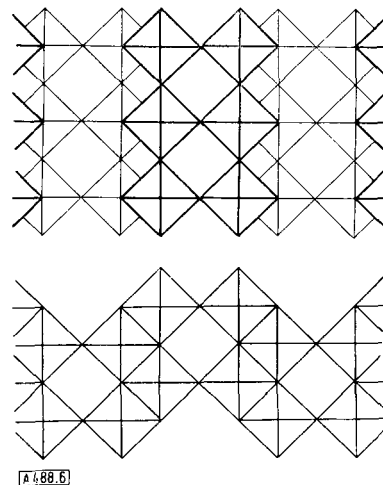


Fig. 6. A particularly simple M_2O_5 structure: V_2O_5 (highly idealized, after [56]).

Such a notation proves to be expedient for understanding structures in which the unit cell contains a multiplicity of O^{2-} octahedra^[40]. It can also be used correspondingly for a structure composed of different O^{2-} coordination polyhedra (type b), particularly octahedra and tetrahedra. If a geometrically simple principle of construction from O^{2-} coordination polyhedra, all possessing the same type of linkage, is required for Nb_2O_5 , $5/2 \text{O}^{2-}$ must be assigned to each metal ion; this condition can be realized, for example, by a structure composed of $[\text{MO}_{3/2} \text{O}_{3/3}]$ octahedra. Such $\text{MO}_{2.5}$ octahedra exist with various types of linkage; one of these possibilities is observed in the case of $\text{B-Nb}_2\text{O}_5$. Here O^{2-} octahedra form pairs through a common edge; the linkage *via* $\text{O}_{3/3}$ corresponds to that in the rutile lattice^[8]; cf. Fig. 7b.

Another geometrically simple arrangement (two Nb_2O_5 per cell) is that in which $[\text{MO}_{3/2} \text{O}_{3/3}]$ octahedra are joined by two perpendicular edges with the neighboring octahedra in such a way that a zigzag chain of octahedra is produced. These chains arranged in parallel would be linked to one another by sharing corners. The resulting constructional principle corresponds to that of the highly idealized^[56] structure of V_2O_5 ^[62] (Fig. 6). A variation of this principle is found in the structure of $\text{P-Nb}_2\text{O}_5$ ^[62a]. It is worth noting that the chains of octahedra mentioned, with $\text{O/Nb} = 2.5$, occur widely as an *additional* constructional element in several forms of Nb_2O_5 and related compounds ($\text{Nb}_{12}\text{O}_{29}$ ^[53],

[58] G. F. Hüttig, E. Zeidler, and E. Franz, Z. anorg. allg. Chem. 231, 104 (1937).

[59] This notation is not completely unambiguous but is adequate to characterize the types of linkage that occur frequently.

[60] This corresponds to the $\text{Nb}_3\text{O}_7\text{F}$ structure [61].

[61] S. Andersson, Acta chem. scand. 18, 2339 (1964).

[62] H. G. Bachmann, F. R. Ahmed, and W. H. Barnes, Z. Kristallogr., Kristallgeomet., Kristallphysik, Kristallchem. 115, 110 (1961).

[62a] F. Laves and W. Petter, 8th Discussion Meeting of the Sektion für Kristallkunde, Marburg 1965.

$\text{Nb}_{25}\text{O}_{62}$ [54,63]; $\text{Nb}_{31}\text{O}_{77}\text{F}$ [17], $\text{Nb}_{17}\text{O}_{42}\text{F}$ [17], $\text{Nb}_3\text{O}_7\text{F}$ [61], and $\text{Nb}_3\text{O}_7\text{Cl}$ [64]). In the majority of such cases (although the X/Nb ratio is close to 2.5) a structure in which “ $\text{MO}_{2.5}$ ” octahedra predominate is avoided, and an arrangement is preferred in which these $\text{MO}_{2.5}$ octahedra are “diluted” to a considerable extent by MO_3 and $\text{MO}_{<2.5}$ octahedra. From another point of view, this means that “block structures” [35] occur. Within the blocks, MO_3 octahedra are joined in the manner of ReO_3 by corners, while the blocks are bound to one another by edge sharing of octahedra ($\text{MO}_{2.5}$ and $\text{MO}_{2.5}$) (cf. also Table 6).

The occurrence of different linkage regions can be regarded to a certain extent as “internal disproportionation” of the structural elements (octahedra), while an actual disproportionation into separated phases is excluded, since the Nb already possesses its maximum charge. If we pass to ternary systems with an X/M ratio of 2.5, there is an additional possibility of an actual disproportionation into phases with simpler structures.

The principle of the structure composed of octahedra with various O/Nb ratios (above, below, and equal to $\text{MO}_{2.5}$) makes it clear that the stoichiometric ratio O/M = 2.5 has no particular structural significance. Consequently, slightly different O/M values near 2.5 can be realized whenever the charge of the lattice units permits such deviations. Related to this is the fact that numerous phases differing from the stoichiometry O/Nb = 2.5 occur in the reduction of Nb_2O_5 [38,39,51–54] and that forms of Nb_2O_5 (H [35], N [65]) belong to “structure-related series” [35,56] whose members have different O/M values. Finally, the O/M ratio can also be varied by passing to ternary compounds rich in Nb_2O_5 [38,39,63,66]. In this way, a direct structural relationship is obtained between the forms of Nb_2O_5 and the related ternary oxides [35,56,63,67].

A discussion of the Nb_2O_5 structures from these idealized geometrical points of view provides information on the possible structure variants and on relationships between them, but permits not statements to be made about the thermodynamic stability of the existing arrangements. However, it should be mentioned that the absolute value of the enthalpy of formation of the Nb_2O_5 modifications decreases in the sequence $\text{B} > \text{T} > \text{H}$, while the molar volume increases in that sequence (cf. Section 7). Such a relationship has been observed frequently with other classes of compounds [68].

B-Nb₂O₅

The crystal structure of this modification has been investigated by Laves *et al.* [8]. It belongs to space group B 2/b, and possesses the smallest molar volume (50.2

[63] Cf. also R. S. Roth and A. D. Wadsley, *Acta crystallogr.* 18, 724 (1965).

[64] H. G. Schnering and W. Mertin, *Naturwissenschaften* 51, 552 (1964).

[65] S. Andersson, personal communication.

[66] A. D. Wadsley, *Acta crystallogr.* 14, 660 (a), 664 (b) (1961).

[67] R. S. Roth, A. D. Wadsley, and S. Andersson, *Acta crystallogr.* 18, 643 (1965).

[68] Cf. H. Biltz: *Raumchemie der festen Stoffe*. Leopold Voss; Leipzig 1934.

cm^3) of all known forms of Nb_2O_5 . The anionic lattice consists of a slightly deformed hexagonal close packing of O^{2-} ; the hexagonal layers run parallel to $(2\bar{1}0)$, with an a-axis in (001) . The octahedral cavities of this packing are two-fifths occupied by Nb. The monoclinic cell contains eight $[\text{MO}_{3/2}\text{O}_{3/3}]$ octahedra occupied by Nb, every two octahedra being linked through an edge to form a pair. Each of the two O^{2-} belonging to a common edge are simultaneously corners of two more octahedra (Fig. 7b); the same type of linkage occurs in the rutile structure (Fig. 7a).

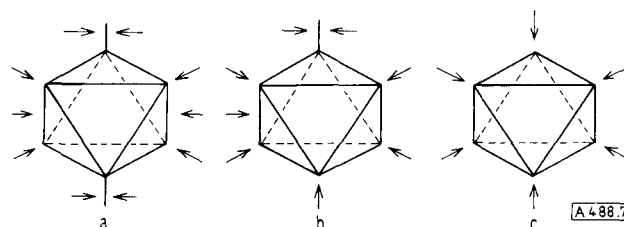


Fig. 7. Types of linkage of O^{2-} octahedra, according to F. Laves [8]. a: Rutile $[\text{MO}_{6/3}]$. b: B- Nb_2O_5 $[\text{MO}_{3/3}\text{O}_{3/2}]$. c: ReO_3 $[\text{MO}_{6/2}]$.

Of the other four O^{2-} of the octahedra under consideration, three are joined by corners (cf. ReO_3 , Fig. 7c) to neighboring octahedra, while one belongs simultaneously to the common edge of another pair of octahedra. The pairs mentioned are arranged parallel to $(2\bar{1}0)$; they are mutually displaced by the width of an octahedron and engage with one another, forming in this way a common “sheet” parallel to (100) with a depth of about $a/2$ (Fig. 8). These sheets are bound to one another only by sharing corners ($\text{O}_{1/2}$). Edge linkages in which $\text{O}_{1/3}$ participate occur only within the sheets.

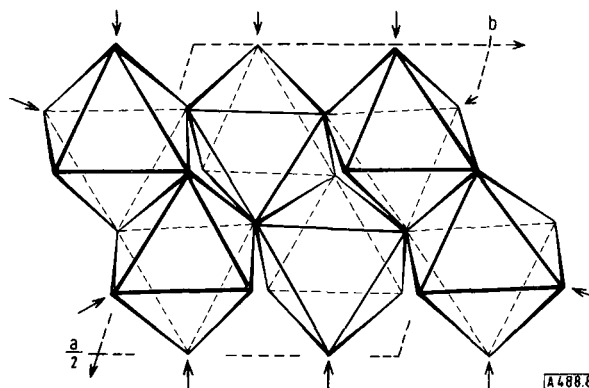


Fig. 8. Structure of B- Nb_2O_5 . Schematic section of the skeleton of O^{2-} octahedra. \uparrow : corner linkage corresponding to ReO_3 .

The numerous unoccupied octahedral sites present in the B- Nb_2O_5 structure obviously offer good possibilities for the incorporation of further metal cations, and this is probably responsible for the fact that B- Nb_2O_5 also incorporates additional Nb under extreme conditions, as follows from the blue color of the preparations (cf. Section 4).

T-Nb₂O₅

The crystal structure of this modification, which has the smallest molar volume (about 53 cm^3) apart from B- Nb_2O_5 , is still unknown. Powder photographs by

the Guinier method show a great similarity to T-Ta₂O₅, which, however, in contrast to T-Nb₂O₅, occurs in several variants^[40,69], and also a particular similarity to Nb₅O₁₂F^[70]. Other relationships exist with U₃O₈ and α-UO₃. It is possible that the compounds mentioned have an almost hexagonal cationic lattice^[71]. Single crystals of T-Nb₂O₅ have been prepared only recently, and are now being investigated^[42].

The crystal structure of the "pseudo-hexagonal"^[5] TT-Nb₂O₅ is perhaps closely related to the structure of T-Nb₂O₅. Since a continuous conversion into the T-form seems to occur when TT-Nb₂O₅ is heated, with some strong reflections being split and many very weak ones being added, the TT-form should probably be regarded as a less ordered precursor of the T-form^[3,6].

H-Nb₂O₅

The crystal structure of this relatively open monoclinic modification (molar volume 58.4 cm³) has recently been determined by Gatehouse and Wadsley^[35]. According to these authors, the structure of the H-form (space group P 2), which contains 28 Nb in the unit cell, is characterized by the occurrence of structural groups related to ReO₃. The idealized H-Nb₂O₅ structure contains two different structural elements which can be regarded as ReO₃-lattice sections of different sizes (and are therefore called "ReO₃ blocks"). Within each of these blocks, the corner linkage of the oxygen octahedra continues uninterrupted (∞) in the direction of growth of the needle (b-axis^[35]); in both directions perpendicular to b, the extension of the blocks is limited to a typical number of octahedra. The two types of blocks occurring can be formulated as [3 × 4 × ∞] and [3 × 5 × ∞]^[35], the number of octahedra in each edge of a block being given. A section in the b-direction of the length of one octahedron diagonal is sufficient to describe the H-Nb₂O₅ structure (and all crystal structures built up correspondingly, cf. N-Nb₂O₅) while the characteristics of the structure are represented by a picture of the extension of the blocks in the (010) plane (Fig. 9). It can be seen that the [3 × 5 × ∞] blocks are displaced with respect to one another and are bound through the narrow sides into "obliquely running chains" of blocks. The spaces between each two of these parallel series of blocks are filled with [3 × 4 × ∞] blocks, the position of which is shifted by b/2 as compared with the [3 × 5 × ∞] blocks. This block skeleton, with 27 octahedrally surrounded niobium cations per cell, contains an additional 4/4 Nb in tetrahedral cavities, half of these cavities being occupied by Nb. Here Nb occurs both in octahedral and in tetrahedral coordination.

The shear planes^[72] envisaged between the ReO₃ blocks are therefore characterized by the fact that here

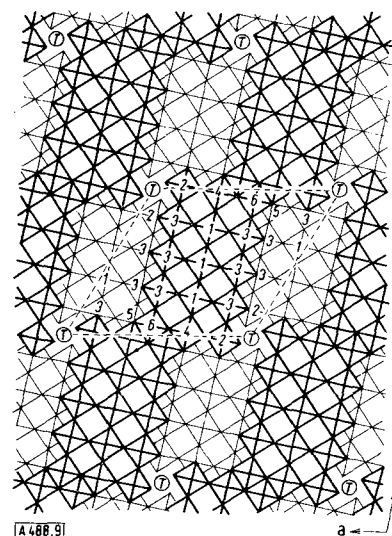


Fig. 9. Structure of H-Nb₂O₅, idealized [35]. For the numbering of the octahedra, see Table 6. The unit cell is indicated by the broken lines.

the oxygen octahedra of adjacent blocks are bound to one another by sharing edges. At these positions, some of the octahedra possess a formal O/M ratio of less than 2.5, so that the stoichiometry M₂O₅ arises from the combination of a total of six types of octahedra differing in their O/M ratio (Table 6).

Table 6. Structure of H-Nb₂O₅.

Linkage symbol	O/Nb	Octahedra per cell	Contribution to the cell content	No. in Fig. 9
[NbO _{6/2}]	3.00	5	Nb ₅ O ₁₅	1
[NbO _{1/1} O _{2/2} O _{3/3}]	3.00 [73]	4	Nb ₄ O ₁₂	2
[NbO _{3/2} O _{3/3}]	2.50	12	Nb ₁₂ O ₃₀	3
[NbO _{2/2} O _{3/3} O _{1/4}]	2.25	2	Nb ₂ O _{4.5}	4
[NbO _{2/2} O _{2/3} O _{2/4}]	2.167	2	Nb ₂ O _{4.33}	5
[NbO _{1/2} O _{4/3} O _{1/4}]	2.083	2	Nb ₂ O _{4.167}	6

(a) Nb participating in octahedra + total O skeleton
= Nb₂₇O₇₀

(b) Nb present in tetrahedra

— Nb

Sum formula

Nb₂₈O₇₀ (Nb₂O₅)

M-Nb₂O₅

The crystal structure of this form is still unknown. The close relationship of the powder diagrams of the M- and H-forms, which agree in a large number of reflections, permits the assumption of a considerable similarity between the two crystal structures. Since, on heating, the M-form apparently changes continuously into the H-form, the diffuse reflections characteristic for M-Nb₂O₅ gradually disappearing, the M-form should perhaps be regarded as a less ordered precursor of the H-form. This is supported by the observation that single

[69] Yu. P. Simanov, A. V. Lapitskii, and E. P. Artemonova, Izv. Mosk. Univ., Ser. fiz.-mat. Nauk. 6, 109 (1954).

[70] S. Andersson and A. Åström, Acta chem. scand. 18, 2233 (1964).

[71] A. F. Wells: Structural Inorganic Chemistry. Oxford University Press, Oxford 1962.

[72] A. D. Wadsley, Proc. Roy. Soc. New South Wales 92, 25 (1958), cf. [66b].

[73] Since in the calculation (Table 6), all O²⁻ were formally reckoned in the octahedron skeleton (a), one type of O²⁻ was considered as belonging only to the octahedron (O_{1/1}) although this O²⁻ simultaneously forms a corner of the neighboring Nb-occupied tetrahedron and therefore would also be counted partially with this Nb. The simplified distribution used here makes it possible to introduce the Nb contained in tetrahedral cavities in the calculation without reference to its environment (b).

crystals of $M\text{-Nb}_2\text{O}_5$ change into single crystals of $H\text{-Nb}_2\text{O}_5$ on heating [44]. X-Ray investigations with single crystals are in progress [28].

A structure in which the arrangement of $H\text{-Nb}_2\text{O}_5$ already exists in two dimensions while there is defective order in the third has been considered by *Holtzberg et al.* [6].

N— Nb_2O_5

The crystal structure of this form has been investigated by *S. Andersson* [74]. According to this work, the structure of the monoclinic N-form can be related to the ReO_3 lattice in a similar manner to that of the H-form. The N-structure contains only *one* type of ReO_3 block: $[4 \times 4 \times \infty]$; these (like the $[3 \times 5 \times \infty]$ blocks of the H-form) are displaced with respect to one another and are linked to form obliquely running chains of blocks (Fig. 10). The positions of neighboring chains of blocks

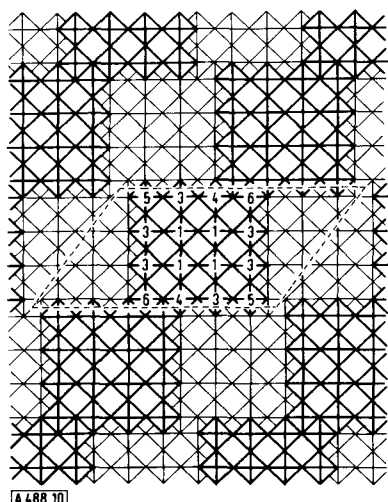


Fig. 10. Structure of N— Nb_2O_5 . Shown in an idealized manner according to *S. Andersson* [74].

differ in the direction perpendicular to the plane of the figure by half an octahedron diagonal, so that edge sharing can occur at each surface of contact between two blocks. Here the stoichiometry is derived by combination of five types of octahedra differing in their formal O/M ratio (numbers 1, 3, 4, 5, and 6 in Fig. 10; cf. Table 6).

[74] These data were kindly made available by Dr. *S. Andersson* [65].

The lattice of N— Nb_2O_5 is closely related to the crystal structures of the compounds TiNb_2O_7 [66a], $\text{Ti}_2\text{Nb}_{10}\text{O}_{29}$ (I) (monoclinic) [66b], and $\text{Nb}_{12}\text{O}_{29}$ (I) (monoclinic) [53, 55] and, like these, contains no tetrahedrally coordinated Nb cations.

P— Nb_2O_5

The structure of this form has been investigated by *Laves et al.* [8, 62a]. The P-structure contains zigzag chains of $\text{MO}_{2.5}$ octahedra like the idealized V_2O_5 -structure, the zigzag chains being parallel and forming sheets. The chains of neighboring sheets, however, in contrast to idealized V_2O_5 , are perpendicular to one another. The lattice constants for the tetragonal P-form (from Guinier photographs) [42] are: $a = 3.90 \text{ \AA}$; $c = 25.5 \text{ \AA}$; $D_{x\text{-ray}} = 4.54 \text{ g/cm}^3$ (cell content $z = 4 \text{ Nb}_2\text{O}_5$); molar volume: 58.5 cm^3 .

7. Thermal and Thermochemical Behavior

Fig. 11 shows the thermal transformations observed so far [76]. The influence of the history of the preparations can be clearly observed. All the conversions mentioned in the figure take place monotropically, and the transition temperatures are therefore due to kinetics.

Consequently, the time of heating is of great importance as follows, for example, from Fig. 12. On the basis of differential thermal analyses, the signs of the heats of transformation are as follows:

- amorphous \rightarrow T, exothermic [6, 75, 77, 78]
- T \rightarrow B, exothermic [75]
- T \rightarrow H, endothermic [75]
- B \rightarrow H, endothermic [75]
- P \rightarrow H, endothermic [75]

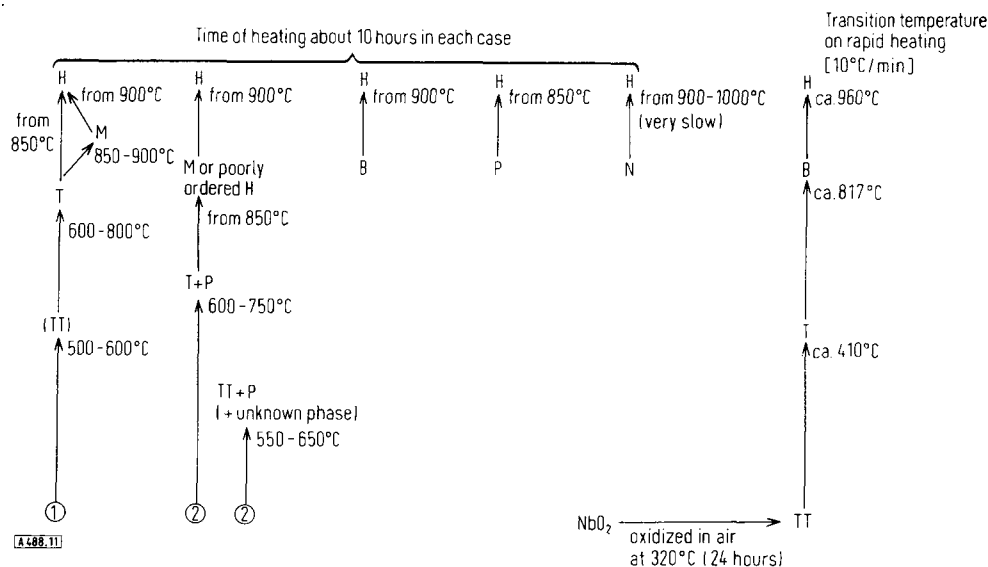


Fig. 11. Conversions of the forms of Nb_2O_5 on heating in air [75]. ① = amorphous "chloride niobic acid" or "sulfate niobic acid", thoroughly washed. ② = amorphous "chloride niobic acid" with a high content of HCl.

[75] Unpublished observations in these laboratories.

[76] The $H \rightarrow I$ -high transformation described by *Shafer and Roy* [3], upon which doubt has been cast by *Reisman and Holtzberg* [4], is not included.

[77] *J. Böhm*, *Z. anorg. allg. Chem.* 149, 217 (1925).

Fig. 13 shows an example of a typical thermogram. The enthalpies of transformation are of the order of one to a few kcal/mole [78].

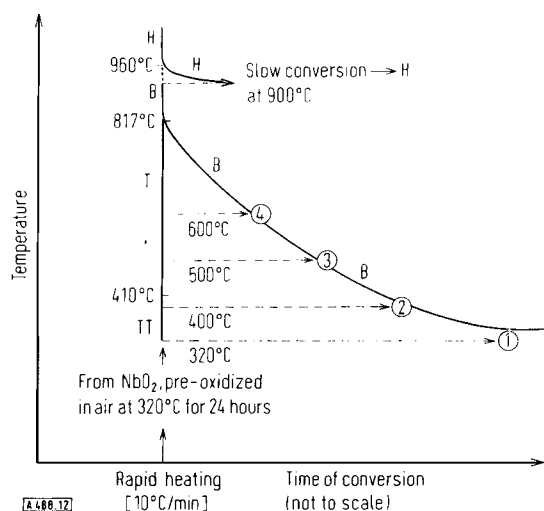


Fig. 12. Influence of time on the conversion of the Nb_2O_5 forms $\text{TT} \rightarrow \text{T} \rightarrow \text{B}$ [75]. Initial preparation: NbO_2 oxidized in air at 320°C ; ① \rightarrow no conversion into $\text{B-Nb}_2\text{O}_5$ in 46 days; ② = predominantly $\text{B-Nb}_2\text{O}_5$ after 14 days; ③ = predominantly $\text{B-Nb}_2\text{O}_5$ after 90 hours, pure $\text{B-Nb}_2\text{O}_5$ after 180 hours; ④ = predominantly $\text{B-Nb}_2\text{O}_5$ after 2 hours.

No indications have so far been found of thermal effects in the $\text{TT} \rightarrow \text{T}$ and $\text{M} \rightarrow \text{H}$ transformations.

It is significant for thermodynamic stability that on isothermal heating [750°C , $P(\text{NbOCl}_3) = 5$ atm and $P(\text{Cl}_2) = 3.5$ atm] tablets of mixtures of the P- and B-forms, or of the T- and B-forms, are converted into the pure B-form [26,45]. In contrast to transport in a temperature gradient, no new formation of nuclei was necessary in this case. It is also important that mixtures of the B- and H-forms are converted into the B-form on isothermal heating [650°C , $P(\text{NbOCl}_3) = 5$ atm and $P(\text{Cl}_2) = 3.1$ atm] [26]. The reversibility of the $\text{B} \rightarrow \text{H}$ transformation was first observed in this way.

The thermodynamic data given in the literature (ΔH° [79]; S° [80]; C_p° [81]) refer to the H-form.

[78] A. V. Lapitskii, Yu. P. Simanov, and E. I. Yarembasch, *Zh. fiz. khim.*, 26, 56 (1952).

[79] G. L. Humphrey, *J. Amer. chem. Soc.* 76, 978 (1954).

[80] E. G. King, *J. Amer. chem. Soc.* 76, 3289 (1954).

[81] R. L. Orr, *J. Amer. chem. Soc.* 75, 2808 (1953).

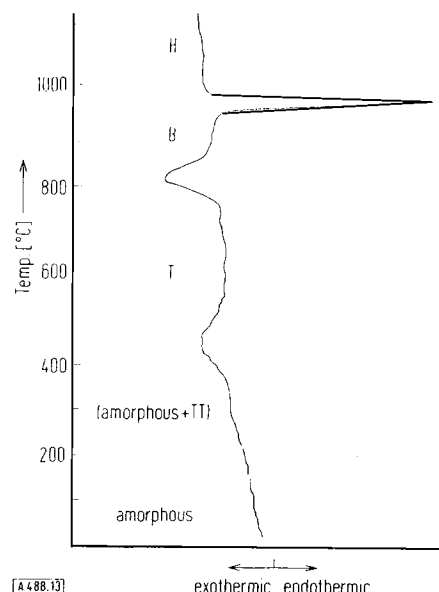


Fig. 13. Differential thermal analysis of the conversions of the Nb_2O_5 forms $\text{amorphous} \rightarrow \text{T} \rightarrow \text{B} \rightarrow \text{H}$. Rate of heating: $10^\circ\text{C}/\text{min}$. Starting material: Nb_2O_5 from NbO_2 oxidized in air at 320°C for a short time.

The observations so far available support the assumption that of all the forms, $\text{B-Nb}_2\text{O}_5$ has the highest absolute value of the enthalpy of formation. Consequently, $\text{B-Nb}_2\text{O}_5$ is thermodynamically stable at low temperatures. As described, the conversion $\text{B} \rightarrow \text{H}$ could be observed at 750°C , while the reverse conversion is realized at 650°C . If the mean (700°C) is taken to be the equilibrium temperature, and if in addition an enthalpy of transformation of 2 kcal/mole is assumed [41], we obtain for the $\text{B} \rightarrow \text{H}$ transformation an entropy increase of 2 cal. The increase in entropy can be understood on the basis of the structure.

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