

Crystal Growth of Some Intermediate Titanium Oxide Phases γ -Ti₃O₅, β -Ti₃O₅, Ti₄O₇ and Ti₂O₃ by Chemical Transport Reactions

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Chemical transport reactions of γ -Ti₃O₅, β -Ti₃O₅, Ti₄O₇ and Ti₂O₃ were performed in closed silica ampoules by using TeCl₄ as a transport medium. Especially, single crystals of γ -Ti₃O₅ were obtained for the first time. The previously unexplained sources of extra oxygen and oxidation introduced into the titanium oxides during transport reactions were discovered in an analysis of 53 experiments. A method is presented which predicts the oxidation state of a transported titanium oxide using empirical equations which take account of the amounts of TeCl₄, H₂O liberated from the wall of the silica ampoule, and the starting material with varied chemical compositions.

The temperature range of coexistence of the γ -Ti₃O₅ and β -Ti₃O₅ crystals was analysed. The twin crystal orientations of the β -Ti₃O₅ phase and an X-ray powder diffraction pattern yielding the refined unit cell parameters of γ -Ti₃O₅ are presented.

The polymorphism and phase transitions of Ti₃O₅ have been extensively studied by several researchers at this institute. In a phase analysis of the titanium-oxygen system it was found that the room temperature modification of a Ti₃O₅ sample prepared at 1150 °C has a monoclinic structure.¹ The crystal structure² which was later called β -Ti₃O₅ is quite different from the orthorhombic pseudobrookite-type of structure (anosovite) assigned to Ti₃O₅ some years earlier by Zhdanov and Rusakov.³ The pseudobrookite structure was found to exist as a high-temperature modification in the binary titanium-oxygen system (α -Ti₃O₅). The rapid reversible α -Ti₃O₅ \rightleftharpoons β -Ti₃O₅ reaction appearing at 150–

160 °C in the strictly binary system could be depressed below room temperature in the presence of impurities, *e.g.* iron in the case of anosovite.

The existence of a new monoclinic modification of Ti₃O₅ (called γ -Ti₃O₅ for the room temperature phase which magnetically transformed to δ -Ti₃O₅ at *ca.* –23 °C) was reported by Åsbrink *et al.*⁴ However, to date, single crystal growth of γ -Ti₃O₅ was unsuccessful; therefore the crystal structure, many physical properties and thermodynamical data still remain unknown.

In the course of the preparative work it was also possible to prepare crystals of β -Ti₃O₅, Ti₂O₃ and of Ti₄O₇, of which the latter is the first member of the homologous series¹ ($4 \leq n \leq 10$) Ti_nO_{2n-1}.

EXPERIMENTAL

Preparation of starting materials. As starting materials Ti₂O₃ and β -Ti₃O₅ powders were used, and these two compounds were carefully prepared in an argon atmosphere by arc-melting mixture of titanium powder (99.9%, Ventron, USA) and titanium dioxide (99.97%, J. T. Baker Chemical Co., USA). The titanium powder and the titanium dioxide were dried before use at 120 °C for *ca.* a week. The stoichiometrically mixed powders for making Ti₂O₃ and β -Ti₃O₅ were compacted at *ca.* 10 kbar to form pellets of 1.2 g each.

After arc-melting each pellet was finely ground in an agate mortar, and the composition was checked by means of X-ray (CuK α ₁) Guinier-Hägg powder photographs taken with a very long exposure time in order to reveal undesired phases. As starting material for further work only the

thoroughly pure samples of Ti_2O_3 (ca. 25 g) and $\beta\text{-Ti}_3\text{O}_5$ (ca. 10 g), respectively, were retained.

Silica ampoule. Schäfer *et al.*⁵ reported that H_2O from the wall of the silica ampoule had a decisive influence on the chemical transport rate of molybdenum and tungsten and of their dioxides and sulfides by means of iodine. According to their experience the water content in the transparent silica ampoule varied between 0.01 wt % for extremely water free silica and 0.10 wt % for ordinary grade silica.

Throughout the experiments ordinary grade transparent silica tubes (99.9 %, Thermal Syndicate Ltd., England) were used, of which the water content was estimated to be ca. 0.10 wt % after cleaning in liquid soap and distilled water and drying at ca. 120 °C for several days. Ordinary grade silica glass was used as its water solubility and diffusion rate⁶ at high temperatures is known. At the same time it seemed to be very difficult to exclude traces of water even from the most water-free silica tube by heating at 900–1000 °C for a couple of days in vacuum.

Furnace. Fig. 1 shows a temperature profile of a horizontal furnace with length $l=500$ mm (inner diameter ID=29 mm, outer diameter OD=250 mm). An effort was made to obtain a very smooth temperature profile and a small temperature gradient in order to make possible the use of long silica ampoules (up to 200 mm) with $\Delta T(=T_2 - T_1) \approx 20$ °C. A Kanthal A-1 helix was carefully wound closer near both ends rather than in the central part of the furnace to yield the small temperature gradient. Sometimes three ampoules as shown in Fig. 1 were inserted for transport reactions simultaneously. The transverse temperature difference was $\lesssim 2$ °C in the furnace.

A chromel-alumel thermocoax (stainless steel or high-melting steel sheath, OD=1.5 mm, SODERN, France) was used with a proportional temperature

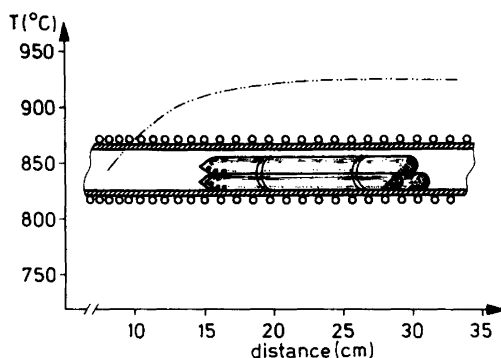


Fig. 1. Inner part of the horizontal furnace with temperature profile indicated (---). Sometimes three ampoules were simultaneously inserted.

regulator (Witronic II, Philips, Holland), which gave a temperature stability of ca. ± 1 °C. At an early stage of the experiments a furnace with two Pt-Pt(Rh) thermocouples at separate temperature control points was used. It was later abandoned, however, because it did not easily yield a very smooth temperature profile.

RESULTS AND DISCUSSION

Parameters to control the oxidation state of the transported crystals.

(1) *Amount of TeCl_4 and previous theories of the extra oxygen and oxidation sources.* Niemysky *et al.*⁷ showed that above 900 °C TeCl_4 is a more effective transport agent for the TiO_2 (rutile) preparation than other halides and halogens. After that work some other oxides⁸⁻¹³ were also transported by using TeCl_4 . Crystals of some intermediate vanadium oxides¹⁴⁻¹⁹ between V_2O_3 and V_2O_5 were also grown by using TeCl_4 . Analogously, Mercier and Lakkis²⁰ obtained the titanium oxides: $\beta\text{-Ti}_3\text{O}_5$, Ti_4O_7 and Ti_5O_9 (Mercier *et al.* only reported the composition Ti_3O_5 and the phase must be $\beta\text{-Ti}_3\text{O}_5$ according to the crystal shape and the temperatures used (ca. 1100 °C) for the chemical transport reaction).

Comparing the above two cases, of vanadium oxides and titanium oxides, there was an essential difference with regard to the compositions of the starting materials and the transported crystals. For the vanadium oxides one observed no composition changes between the starting material and the transported crystals. Even when composition changes were observed in some cases, they were usually small or within the range of homogeneity. However, for the titanium oxide transport reactions one always needed a starting material with a lower oxidation state than that of the grown crystals. In order to grow *e.g.* $\beta\text{-Ti}_3\text{O}_5$ one needed Ti_2O_3 as starting material; similarly, Ti_3O_5 and Ti_4O_7 were required for the growth of Ti_4O_7 and Ti_5O_9 , respectively. This phenomenon was explained by a quasiequilibrium²⁰ in the reaction ampoule; it means that the oxygen partial pressures in the hotter zone (at T_2 , *e.g.* Ti_3O_5 as a starting material with the lower oxidation state) and in the colder zone (at T_1 , *e.g.* transported crystals of Ti_4O_7 with the higher oxidation state) are the same and are equal to the corresponding equilibrium pressures above the two solid oxides, at their respective temperatures.

According to the above explanation the used temperatures T_1 and T_2 are the most significant parameters, together with the oxidation state of the starting material, determining the oxygen partial pressures in the two zones, and therefore they determine the oxidation state of the transported crystals.

No satisfactory explanation has been published which accounts for the extra oxygen and oxidation sources in the chemical transport reactions of the titanium oxides, even though the chemical transport direction and main gas species (TiCl₄, TeOCl₂, TeCl₄, TeCl₂ and Cl₂) involved in the system TiO₂:TeCl₄ were established by matrix isolation infrared spectroscopy.²¹

Recently, Since *et al.*²² offered a new hypothesis, stating that the extra oxygen source was probably water from the wall of the silica ampoule and the hygroscopic transport agent TeCl₄.

The experimental results from 53 careful runs (*cf.* Table 3), initially intended for the γ -Ti₃O₅ and β -Ti₃O₅ preparation by chemical transport reactions, showed that water could not be the sole oxidizing agent, and that a completely new explanation was required (*cf.* runs Nos. 29 in Table 1; 34, 36 and 52 in Table 2). Tables 1 and 2 show some typical experimental parameters: special attention was paid to water possibly adsorbed on the starting material and on the inside surface of the silica ampoule or to water in TeCl₄. The tellurium tetrachloride was stored, weighed and charged into the silica ampoule in a dry box. After charging, the

hygroscopic TeCl₄ was carefully dried by gentle heating in vacuum (10^{-6} – 5×10^{-5} Torr, ≥ 15 hours) just until sublimation of TeCl₄ occurred. The transport reaction of each pair of runs: Nos. 28 and 29, 40 and 41 in Table 1 were performed simultaneously as shown in Fig. 1 in order to ensure identical temperature conditions.

When the concentration of TeCl₄ (99.99 %, Mitsuwa Chemicals, Japan) was 4.0 mg/ml or less, dark violet Ti₂O₃ crystals were transported to the colder zone, while run No. 28 yielded well-developed single phase crystals of γ -Ti₃O₅ with 7.2 mg/ml. For the two runs Nos. 28 and 29 possible H₂O amounts liberated from the wall of the silica ampoules should be exactly equal, because each pair of the ampoules used in runs Nos. 28 and 29, 40 and 41 was prepared from the same length of silica tube.

Analogously, a comparison between runs Nos. 40 and 41 and the results of further experiments with different silica ampoule volumes, but with the same concentration (mg/ml) of TeCl₄ showed that the oxidation state of the transported crystals was dependent on the input amount of TeCl₄, even though the higher concentration of TeCl₄ gives the larger amount of TeCl₄ with a similar ampoule volume (discussed later). The oxidation state of the transported titanium oxide crystals will increase with increasing amount of TeCl₄. This oxidizing effect of the transport agent TeCl₄ was also observed on the chemical transport of NbO₂ and NbO_{2.417}.²³

(2) *Amounts of H₂O and of starting materials.* Table 2 shows the influence of the silica ampoule

Table 1. Influence of the amount of TeCl₄ on the oxidation state of the transported crystals. Each pair of runs Nos. 28 and 29, 40 and 41 was simultaneously performed, as shown in Fig. 1. The abbreviations *l*, ID and wt stand for length, inner diameter and weight, respectively. $T_2 \rightarrow T_1$ indicates the direction of the chemical transport.

Run No.	Starting material (g)	Ampoule			TeCl ₄ (mg/ml)	Temp. (°C)		Transported crystals	Residue	Transport time (day)
		<i>l</i> (mm)	ID (mm)	wt (g)		$T_2 \rightarrow T_1$				
29	Ti ₂ O ₃ 0.30	130	10.0	12.7	4.0	900	880	Ti ₂ O ₃	Ti ₂ O ₃	16
	β -Ti ₃ O ₅ 0.10								γ -Ti ₃ O ₅ β -Ti ₃ O ₅	
28	Ti ₂ O ₃ 0.30	130	10.0	12.7	7.2	900	880	γ -Ti ₃ O ₅	γ -Ti ₃ O ₅	16
	β -Ti ₃ O ₅ 0.10								β -Ti ₃ O ₅	
40	Ti ₂ O ₃ 0.30	145	10.0	13.5	7.8	960	910	γ -Ti ₃ O ₅	γ -Ti ₃ O ₅	24
	β -Ti ₃ O ₅ 0.10								β -Ti ₃ O ₅	
41	Ti ₂ O ₃ 0.30	145	10.0	13.5	10.1	960	910	γ -Ti ₃ O ₅ Ti ₄ O ₇	β -Ti ₃ O ₅ Ti ₄ O ₇	24
	β -Ti ₃ O ₅ 0.10									

Table 2. Influence of the silica ampoule wt (H_2O content ≈ 0.001 wt) and the amount of starting material with a certain composition on the oxidation state of the transported crystals.

Run No.	Starting material (g)		Ampoule			TeCl ₄ (mg/ml)	Temp. (°C)		Transported crystals	Residue	Transport time (day)
			l (mm)	ID (mm)	wt (g)		T ₂ →	T ₁			
36	Ti ₂ O ₃	0.30	95	10.3	7.5	7.0	940	910	Ti ₂ O ₃	Ti ₂ O ₃	20
	β-Ti ₃ O ₅	0.10							β-Ti ₃ O ₅	γ-Ti ₃ O ₅	
34	Ti ₂ O ₃	0.60	120	10.2	9.3	6.0	935	910	Ti ₂ O ₃	Ti ₂ O ₃	28
	β-Ti ₃ O ₅	0.20							γ-Ti ₃ O ₅	β-Ti ₃ O ₅	
35	Ti ₂ O ₃	0.30	130	10.2	10.1	8.0	930	908	γ-Ti ₃ O ₅	γ-Ti ₃ O ₅	24
	β-Ti ₃ O ₅	0.10							β-Ti ₃ O ₅	β-Ti ₃ O ₅	
52	Ti ₂ O ₃	0.50	140	10.0	10.7	6.6	1005	920	Ti ₂ O ₃	Ti ₂ O ₃	9
32	Ti ₂ O ₃	0.30	140	10.3	11.0	6.0	955	925	γ-Ti ₃ O ₅	γ-Ti ₃ O ₅	8
	β-Ti ₃ O ₅	0.10							γ-Ti ₃ O ₅	β-Ti ₃ O ₅	
49	Ti ₂ O ₃	0.40	165	10.0	12.6	7.6	985	900	γ-Ti ₃ O ₅	γ-Ti ₃ O ₅	21
19	Ti ₂ O ₃	0.30	150	9.5	14.0	8.5	900	800	Ti ₄ O ₇	γ-Ti ₃ O ₅	7
	β-Ti ₃ O ₅	0.20							β-Ti ₃ O ₅	Ti ₄ O ₇	

dimensions on the oxidation state of the transported crystals. The length of the silica ampoules was varied; accordingly the weight (wt) of the silica ampoules was also varied, while the concentration of TeCl₄ was kept between 6.0–8.5 mg/ml. Under these conditions 18 successful runs of single phase γ-Ti₃O₅ growth were performed (*cf.* Table 3).

Comparing run No. 28 in Table 1 with run No. 36 in Table 2, the concentrations of TeCl₄ were almost equal to 7 mg/ml in both cases (which should give almost the same total pressure with similar temperatures), run No. 28 yielded high-quality γ-Ti₃O₅ crystals, whereas single phase Ti₂O₃ was obtained

in run No. 36. One of the significant differences between the experimental parameters of the two runs was the length of the silica ampoules, which was generally expected to influence only the transport rate.²⁴ The total amounts of TeCl₄ for the two runs of Nos. 28 and 36 were 73 mg and 55 mg, respectively. This difference should also be significant, as discussed previously; and the decisive significance of the relation between the amounts of H₂O and TeCl₄ will be quantitatively discussed later.

Runs Nos. 32 and 34 in Table 2 were performed at similar temperatures and with the same concentration of TeCl₄, 6.0 mg/ml. Run No. 32 yielded single phase γ-Ti₃O₅, while No. 34 transported single phase Ti₂O₃ from twice the amount of starting material with the same composition.

The previous results and a further comparison between run No. 52 and run No. 49 clearly suggested that the oxidation state of the transported crystals was essentially dependent on the silica ampoule dimensions, the total amount of starting materials with a certain chemical composition and the input amount of TeCl₄, but not primarily dependent on the total pressure in the ampoule.

Table 3. Specification of the 53 transport runs.

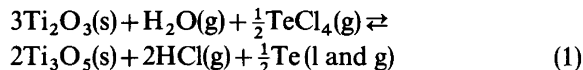
Transported crystals	Total No. of runs
γ-Ti ₃ O ₅	18
β-Ti ₃ O ₅	3
Ti ₄ O ₇	11
Ti ₂ O ₃	12
γ-Ti ₃ O ₅ + Ti ₄ O ₇	4
γ-Ti ₃ O ₅ + Ti ₂ O ₃	1
β-Ti ₃ O ₅ + Ti ₂ O ₃	4

The oxidation state of the transported crystals was raised by increasing the input amount of TeCl_4 and the ampoule weight; the oxidation state was lowered by increasing the total amount of starting material.

In all 53 runs the ampoules, which had been quenched in water, emitted strongly concentrated white fumes of HCl upon breaking after the transport reaction. Addition of a water volume equal to that of the ampoule yielded a HCl solution with $\text{pH} \approx 1$. However, in the chemical transport reactions of V_2O_5 (starting material = V_2O_5 , $T_1 = 950^\circ\text{C}$ and $T_2 = 1050^\circ\text{C}$) performed under the same experimental conditions, neither these white fumes of HCl nor Te metal (discussed below) was observed. The hydrogen source of HCl must be H_2O from the wall of the silica ampoule, because the starting materials and TeCl_4 were carefully dried before use, and especially the starting materials had no contact with hydrogen gas during the preparation. Exactly the same phenomenon was observed by Mercier *et al.*²⁰ in the chemical transport reactions of titanium oxides by using TeCl_4 ; however, they assumed the source of hydrogen to be their starting materials, which were obtained by reduction of TiO_2 by hydrogen gas.

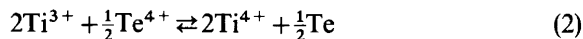
A large amount of silvery white tellurium metal (b.p. = $989.8 \pm 3.8^\circ\text{C}$) was always observed in the silica ampoule after quenching in water. Concerning the observed liquid and solid components in the quenched ampoule, tellurium metal in the shapes of thin plates, spheres and crystals appeared in significant amounts besides the titanium oxides (including the starting materials and transported crystals). The major portion of the Te metal was found in the colder zone, which was raised 1–2 mm above the hotter zone in order to preclude contact between liquid Te and the growing titanium oxide crystals. When ca. 8 mg $\gamma\text{-Ti}_3\text{O}_5$ was transported with $T_1 = 910^\circ\text{C}$ and $T_2 = 955^\circ\text{C}$, ca. 17 mg Te metal (ca. 41 % of the total input as TeCl_4) was observed in the colder zone. The transported Te metal was usually 40–50 % of the input amount. The material was not TeO_2 (m.p. = 733°C , b.p. = 1245°C), as earlier assumed in analogy with the rutile transport.⁷

One may now summarize the experimental results in the stoichiometric equation (1) for the $\gamma\text{-Ti}_3\text{O}_5$ and $\beta\text{-Ti}_3\text{O}_5$ transports using TeCl_4 as transport medium and a charge of Ti_2O_3 or a mixture of Ti_2O_3 and $\beta\text{-Ti}_3\text{O}_5$ powders as starting material.



Eqn. (1) is not intended to explain the whole transport system. It excludes many equilibrium reactions of carrier gases (TiCl_4 , TiCl_3 , TeOCl_2 and *etc.*)²¹ and of thermal dissociation,²⁵ *e.g.*, $\text{TeCl}_4(\text{g}) \rightleftharpoons \text{TeCl}_2(\text{g}) + \text{Cl}_2(\text{g})$. However, the eqn. (1) is clearly able to explain the extra oxygen and oxidation sources and to quantitatively clarify the relationship between input and output in the closed transport system of a silica ampoule. Furthermore it is capable of predicting the oxidation state of the transported crystals (discussed later in detail); this capability is most important in order to obtain a desired phase in a strictly controlled way.

When one considers eqn. (1) as a *redox* reaction, one may formulate a *net redox* reaction, eqn. (2).



Hereby one can clearly see Te^{4+} (TeCl_4) as an oxidizer, and one may understand the decisive importance of the total input amount of TeCl_4 for the oxidation state of the transported crystals, as discussed previously (*cf.* Table 1). However, it seems hardly believable that TeCl_4 should actively function as oxidizer without the coexistence of H_2O liberated from the wall of the silica ampoule as an extra oxygen source.

Coexistence of $\gamma\text{-Ti}_3\text{O}_5$ and $\alpha\text{-Ti}_3\text{O}_5$ ($\beta\text{-Ti}_3\text{O}_5$). Single crystals of $\gamma\text{-Ti}_3\text{O}_5$ were obtained in a single phase transport to the colder zone whose temperature was varied within $T_1 = 800\text{--}930^\circ\text{C}$ with $\Delta T = 15\text{--}100^\circ\text{C}$. When one inspected the residue in the hotter zone (at T_2) after successful transport reactions, $\gamma\text{-Ti}_3\text{O}_5$ and $\alpha\text{-Ti}_3\text{O}_5$ crystals were always found to have developed together in the temperature range $900^\circ\text{C} \leq T_2 \leq 990^\circ\text{C}$. The $\gamma\text{-Ti}_3\text{O}_5$ and $\beta\text{-Ti}_3\text{O}_5$ crystals could be easily distinguished since they have completely different shapes, as shown in Fig. 2. However, in the residue

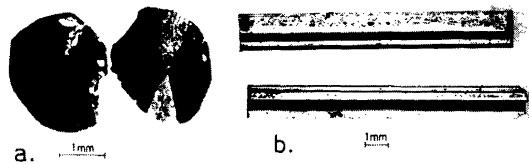


Fig. 2. Photograph of two modifications of the Ti_3O_5 crystals. a, $\gamma\text{-Ti}_3\text{O}_5$, black; b, $\beta\text{-Ti}_3\text{O}_5$, black.

the crystal quality of γ - Ti_3O_5 is always much higher than that of β - Ti_3O_5 .

In run No. 49 in Table 2, with $T_2=985^\circ\text{C}$, the residue consisted mostly of β - Ti_3O_5 crystals; only 2–3 % was γ - Ti_3O_5 crystals, observable under the microscope, but hardly detectable by X-ray powder diffraction. The lower temperature limit of γ - Ti_3O_5 and α - Ti_3O_5 coexistence in the hotter zone seems to be slightly below 900°C , because the β - Ti_3O_5 crystals were still observed at $T_2=900^\circ\text{C}$. No experiment was done at $T_2 < 900^\circ\text{C}$ due to too slow water diffusion⁶ into the reaction room of the ampoule. A consequence of the slow water diffusion, combined with a large transport rate (≥ 3 mg/h), is a two-phase transport or varied oxygen content in the single phase transported crystals, as the transport system takes much longer time (≥ 2 day) to reach a state of equilibrium. Meanwhile, a major part of the crystals would already be transported. On the other hand, at $T_2=990^\circ\text{C}$ only β - Ti_3O_5 crystals were observed. One may draw a borderline at *ca.* 940°C : at that temperature the

amounts of γ - Ti_3O_5 and β - Ti_3O_5 crystals in the residue were equal.

The coexistence temperature range in the colder zone seemed to be very narrow, as no trace of β - Ti_3O_5 crystals was found below $T_1=930^\circ\text{C}$; and at that temperature well-formed crystals of γ - Ti_3O_5 appeared regularly. When the two phases γ - Ti_3O_5 and Ti_4O_7 were transported simultaneously as in run No. 41 in Table 1, the temperature range of coexistence was also narrow – no trace of γ - Ti_3O_5 was found in the hotter zone at $T_2=960^\circ\text{C}$.

Prediction of the yield. Table 3 shows the results of the 53 experimental runs, which thoroughly demonstrated the decisive influence of the amounts of TeCl_4 and H_2O liberated from the silica ampoules upon the oxidation state of the transported crystals. Table 4 lists quantitative comparisons between the input (in) amounts of H_2O and TeCl_4 and those calculated (calc) to fully oxidize the starting material to Ti_3O_5 according to the empirical equation (1). The input amount of H_2O for the transport system was taken to be 0.10 wt % of the used silica

Table 4. Different combinations of Q_1 and Q_2 for the single phase transports of Ti_2O_3 , γ - Ti_3O_5 , Ti_4O_7 or for the two-phase transports of γ - Ti_3O_5 and Ti_4O_7 . See text for explanation of symbols Q_1 , Q_2 , $\text{H}_2\text{O}(\text{in})$, $\text{H}_2\text{O}(\text{calc})$, $\text{TeCl}_4(\text{in})$ and $\text{TeCl}_4(\text{calc})$.

Run No.	$\text{H}_2\text{O}(\text{in})$ (mg)	$\text{H}_2\text{O}(\text{calc})$ (mg)	Q_1	$\text{TeCl}_4(\text{in})$ (mg)	$\text{TeCl}_4(\text{calc})$ (mg)	Q_2
Ti_2O_3						
29	12.7	12.5	1.02	41	93.7	0.44
34	9.3	25.0	0.37	59	187.4	0.31
36	7.5	12.5	0.60	55	93.7	0.59
52	10.7	20.9	0.51	73	156.0	0.47
γ - Ti_3O_5						
11	9.6	10.2	0.94	66	76.2	0.87
28	12.7	12.5	1.02	73	93.7	0.78
30	13.7	12.5	1.10	77	93.7	0.82
32	11.0	12.5	0.88	70	93.7	0.75
35	10.1	12.5	0.81	85	93.7	0.91
40	13.5	12.5	1.08	89	93.7	0.95
43	11.0	14.2	0.77	92	106.2	0.87
45	10.3	15.9	0.65	90	118.7	0.76
49	12.6	16.7	0.75	99	125.0	0.79
γ - $\text{Ti}_3\text{O}_5 + \text{Ti}_4\text{O}_7$						
41	13.5	12.5	1.08	115	93.7	1.23
Ti_4O_7						
17	13.1	10.4(20.6)	1.26(0.64)	88	78.1(154.7)	1.13(0.57)
18	14.0	10.2(19.3)	1.37(0.73)	85	76.2(144.4)	1.12(0.59)
19	14.0	12.5(22.8)	1.12(0.61)	90	78.1(170.6)	1.15(0.53)

ampoule. Table 4 shows only runs with different combinations of the amounts of H₂O, TeCl₄ and starting materials of varied chemical compositions.

As starting material Ti₂O₃ or a mixture of Ti₂O₃ and β -Ti₃O₅ powders was used. As shown in Tables 1 and 2, single phase transport of the γ -Ti₃O₅ crystals only occurred when the residue was completely oxidized to Ti₃O₅.

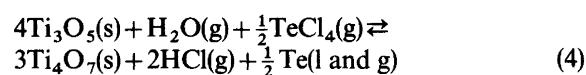
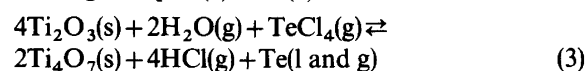
Table 4 lists the two ratios $Q_1 = m_{\text{H}_2\text{O}(\text{in})}/m_{\text{H}_2\text{O}(\text{calc})}$ and $Q_2 = m_{\text{TeCl}_4(\text{in})}/m_{\text{TeCl}_4(\text{calc})}$ with the $m_{(\text{calc})}$ -values derived from eqn. (1). The average values $Q_1 = 0.80$ and $Q_2 = 0.80$ were calculated from 18 successful single phase transport reactions of γ -Ti₃O₅ crystals (cf. Table 3) with an average temperature of 926 °C. One can hereby predict the oxidation state of the transported crystals by combining these two empirical values of Q_1 and Q_2 . When both Q_1 and Q_2 are within 0.80 ± 0.15 , one should obtain single phase γ -Ti₃O₅ or β -Ti₃O₅, assuming optimal temperature control.

In runs Nos. 28, 30 and 40 in Table 4, yielding γ -Ti₃O₅, Q_1 was slightly larger than the upper limit 0.95. However, one could still obtain the single phase transport of γ -Ti₃O₅ as long as the other ratio was kept within the range 0.80 ± 0.15 . It is quite reasonable to assume that the oxidation state of the transport system is determined by the smallest of the two values Q_1 and Q_2 .

Twelve runs yielded single phase Ti₂O₃ (cf. Table 3) when one or both of Q_1 and Q_2 were smaller than the lower limit 0.65. The yield of single phase Ti₂O₃ from the starting material, Ti₂O₃ or a mixture of Ti₂O₃ and β -Ti₃O₅ (≤ 50 wt % of the charge), was completely unexpected judged from previous theories^{20,22} about the extra oxygen and oxidation sources. However, the empirical values of Q_1 and Q_2 based on eqn. (1) quantitatively predicted the yield of Ti₂O₃ crystals when the average oxidation state of the transport system was lower than Ti₃O₅. Two phase transport of γ -Ti₃O₅ and Ti₂O₃ was especially rare. In only one of the 53 runs this happened (cf. Table 3), and then it was probably caused by the back transport step with a large $\Delta T > 200$ °C, a large temperature oscillation ($\approx \pm 5$ °C) and an uneven temperature profile of the furnace. On the other hand, two phase transport of β -Ti₃O₅ and Ti₂O₃ was rather frequent (cf. Table 3). However, the β -Ti₃O₅ crystals always grew in the vicinity of the hotter zone and Ti₂O₃ in the colder zone, with $T_1 = 1060 - 1070$ °C, $\Delta T = 25 - 70$ °C and $\text{TeCl}_4(\text{in}) = 1.5 - 4$ mg/ml. When the amount of β -Ti₃O₅ (300 mg) was three times that of Ti₂O₃

(100 mg) or more in the starting material, only β -Ti₃O₅ crystals were transported to the hotter zone. This reverse transport was also observed by Westphal *et al.*²¹ with similar mean temperatures ≥ 1080 °C and $\text{TeCl}_4(\text{in}) = 2$ mg/ml in the rutile transport reactions.

Analogously one can predict the yield of Ti₄O₇ crystals when both Q_1 and Q_2 are slightly larger than the upper limit 0.95, derived for the single phase transport of γ -Ti₃O₅. For the single phase transport of Ti₄O₇, the additional values of Q_1 and Q_2 within parentheses in Table 4 were calculated on the assumption that the whole starting material of Ti₂O₃ and β -Ti₃O₅ was oxidized to Ti₄O₇ according to eqns. (3) and (4).



After single phase transport of Ti₄O₇ as well as Ti₂O₃ one always observed a large quantity of γ -Ti₃O₅ and β -Ti₃O₅ crystals in the residue together with the phase of the transported oxide, as shown in Tables 1 and 2. Surprisingly, the single phase transport of Ti₂O₃ was possible with the residue consisting of up to 80–90 % Ti₃O₅ crystals. It was not possible to find a satisfactory explanation of the fact that the average oxidation state differed between transported crystals and residue in the Ti₂O₃ and Ti₄O₇ transport reactions, whereas the single phase transport of γ -Ti₃O₅ invariably required the residue to be pure Ti₃O₅. This sensitivity to the oxidation state in the transport system might be the reason why it was difficult to find optimal parameters by trial and error for the single phase transport of γ -Ti₃O₅ crystals, without a knowledge of the chemical equation (1) and the related values of Q_1 and Q_2 .

Correcting the values of Q_1 and Q_2 for the Ti₂O₃ and Ti₄O₇ growth by taking account of the amount of Ti₃O₅ in the residue, one obtains new values within the limit 0.80 ± 0.15 .

With TiO₂ (rutile), the highest oxidation state among the titanium oxides, one did not observe any difference in oxidation state between the starting material (TiO₂) and the transported crystals (TiO₂). However, the oxygen content of the transported crystals might be changed to the upper phase boundary within the homogeneity range, according to the oxidation mechanism provided by H₂O and TeCl₄.

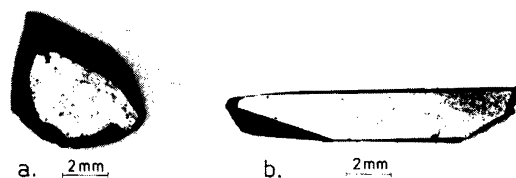


Fig. 3. Photograph of the transported crystals. a, Ti_2O_3 , dark violet; b, Ti_4O_7 , black.

After establishing eqn. (1) and the related values of Q_1 and Q_2 derived from the 53 runs, seventeen further test runs (not included in Table 3) of the $\gamma\text{-Ti}_3\text{O}_5$ transport were performed with varied amounts and composition of the starting materials, utilizing the presented method to predict the yield. High quality crystals of single phase $\gamma\text{-Ti}_3\text{O}_5$ were invariably transported when the amounts of H_2O and TeCl_4 were adjusted to place Q_1 and Q_2 within 0.80 ± 0.15 . The concentration of TeCl_4 was kept within 6–9 mg/ml in order to produce a suitable transport rate and crystal quality.

Similar chemical equations and related values of Q_1 and Q_2 for the higher titanium oxides of the homologous series $\text{Ti}_n\text{O}_{2n-1}$ will surely serve to optimize the transport parameters, of which the combinations are otherwise numerous and often laborious to check. In such a manner it should be possible to obtain a desired phase, crystal quality and transport rate by choosing an adequate composition and amount of the starting material, dimensions of silica ampoule (not only l and ID but also masses are significant), total amount of TeCl_4 and temperature interval.

Description of the transported crystals. The typical crystals of $\gamma\text{-Ti}_3\text{O}_5$ and $\beta\text{-Ti}_3\text{O}_5$ are shown in Fig. 2, and the crystals of Ti_2O_3 and Ti_4O_7 are seen in Figs. 3a and 3b, respectively. The crystals of the $\gamma\text{-Ti}_3\text{O}_5$ and $\beta\text{-Ti}_3\text{O}_5$ and Ti_4O_7 phases are black. The crystals of Ti_2O_3 are dark violet. Further investigations of the hexagonal Ti_2O_3 or triclinic Ti_4O_7 crystals were not performed, because the primary interest was in the monoclinic $\gamma\text{-Ti}_3\text{O}_5$ and $\beta\text{-Ti}_3\text{O}_5$ phases.

The $\beta\text{-Ti}_3\text{O}_5$ crystals have the shape of well-developed rectangular plates with typical dimensions of *ca.* $0.5 \times 1.5 \times 10 \text{ mm}^3$. The longest edge (*ca.* 10 mm) was always the unique monoclinic b axis. A Weissenberg zero-level film with b as the rotation axis revealed twin formation, although the pieces of material looked like beautiful single

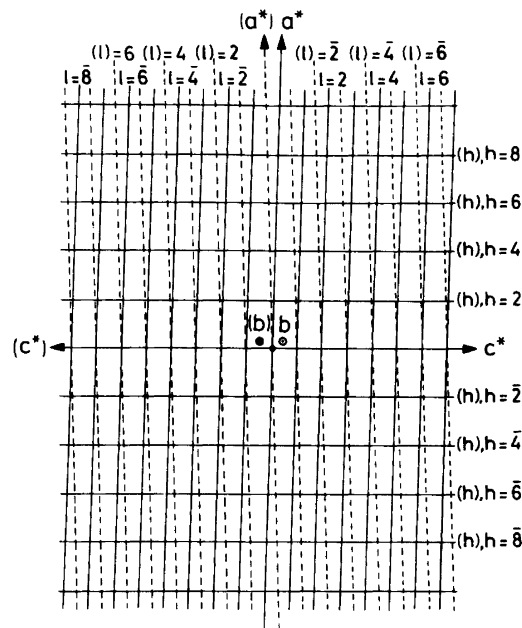


Fig. 4. Twin crystal orientations of the transported $\beta\text{-Ti}_3\text{O}_5$ crystals (*cf.* Fig. 2). One orientation of an $h 0 l$ lattice plane is drawn with solid lines ($c^* a^* b$) and the other is indicated with broken lines. The indices and the signs of the axes for the latter orientation are given within parentheses ($(c^*) (a^*) (b)$). \odot indicates that the positive direction of the unique monoclinic b axis is from the paper to the reader, and \otimes denotes the opposite direction (right-handed system). The horizontal lines of h and (h) indices are identical with each other. The b and (b) , c^* and (c^*) orientations are coincident, respectively; however the directions are opposite. $\beta^* = 88.45^\circ$.

crystals. Fig. 4 shows the twin orientations in $\beta\text{-Ti}_3\text{O}_5$. The ratios of $I(h 0 l)$ and $I(h 0 \bar{l})$ intensities were almost equal even for a small fragment broken from a large "crystal", indicating that the twin formation is of the intergrowth type.

A preliminary study of the structural transition to $\alpha\text{-Ti}_3\text{O}_5$ (transition point (t_T) $\approx 150\text{--}160^\circ\text{C}$) was performed. When $\beta\text{-Ti}_3\text{O}_5$ was very slowly heated in a stream of hot nitrogen gas,²⁶ the twin crystals converted to a single crystal of $\alpha\text{-Ti}_3\text{O}_5$. However, the crystals used to crack when cooled again through t_T . The reason for cracking could be either a too large change of the unit cell volume in the first-order transition, or twin formation, or both. Therefore efforts to transport single crystals of $\beta\text{-Ti}_3\text{O}_5$ are now in progress by sharply optimizing the transport conditions.

Table 5. X-Ray powder diffraction pattern for the γ -Ti₃O₅ phase at 24 °C. CuK α ₁ ($\lambda=1.540598$ Å),²⁸ Si ($a=5.431065$ Å)²⁸ as an internal standard. $\Delta 2\theta=2\theta_{\text{obs}}-2\theta_{\text{calc}}$. Figure of merit $F_N(=\frac{1}{|\Delta 2\theta|} \times \frac{N}{N_{\text{poss}}})$ was defined by Smith *et al.*³¹ N_{poss} = number of possible reflexions up to N th observed reflexion. The refined unit cell parameters are shown in Table 6.

d_{obs} (Å)	I_{obs}	hkl	$2\theta_{\text{obs}}$ (°)	$\Delta 2\theta$	$F_N(\Delta 2\theta , N_{\text{poss}})$
4.68459	33	2 0 0	18.9288	0.0159	63 (0.0159, 1)
4.46147	12	1 1 0	19.8845	0.0070	87 (0.0115, 2)
3.37590	66	0 0 2	26.3793	0.0076	59 (0.0102, 5)
3.32780	11	-2 0 2	26.7676	0.0055	74 (0.0090, 6)
2.93048	62	-1 1 2	30.4793	0.0013	96 (0.0075, 7)
2.66133	100	3 1 0	33.6489	-0.0001	108 (0.0062, 9)
2.53663	42	0 2 0	35.3562	0.0104	103 (0.0068, 10)
2.50509	11	1 1 2	35.8164	-0.0012	119 (0.0061, 11)
2.46533	58	-3 1 2	36.4140	0.0038	127 (0.0059, 12)
2.38284	6	2 0 2	37.7214	0.0009	143 (0.0054, 13)
2.23997	63	1 2 1	40.2278	-0.0048	122 (0.0053, 17)
2.23656		-4 1 1	40.2916	0.0113	115 (0.0058, 18)
2.14593	33	-2 1 3	42.0724	-0.0094	107 (0.0061, 20)
2.02852	24	0 2 2	44.6344	0.0002	112 (0.0057, 22)
1.75906	51	5 1 0	51.9401	0.0007	91 (0.0053, 31)
1.73705	56	2 2 2	52.6484	-0.0017	98 (0.0051, 32)
1.72160	12	4 2 0	53.1580	0.0081	94 (0.0053, 34)
1.67143	76	-1 1 4	54.8855	-0.0086	84 (0.0055, 39)
1.64795	28	-6 0 2	55.7346	-0.0114	75 (0.0058, 44)
1.53009	8	-1 3 2	60.4545	0.0040	69 (0.0057, 51)
1.48778	16	3 3 0	62.3625	-0.0049	68 (0.0057, 54)
1.45081	67	-3 3 2	64.1383	-0.0038	67 (0.0056, 59)
1.44009	10	2 0 4	64.6733	0.0051	67 (0.0056, 61)
1.41036	18	-6 0 4	66.2093	0.0049	70 (0.0055, 62)
1.39156	37	-4 2 4	67.2215	0.0026	69 (0.0054, 67)
1.38924		5 1 2	67.3490	-0.0024	72 (0.0053, 68)

Single crystals of γ -Ti₃O₅ were 1–3 mm in both length and width, and 0.5–1.5 mm in thickness after transport periods of 7–28 days. The two best developed crystal faces were (0 0 $\bar{1}$) and (1 0 0). Their intersection formed a very sharp edge parallel to the unique monoclinic b axis. The angle between the faces was easily confirmed under the microscope to be $\beta^* \approx 70.1^\circ$.

Refinement of unit cell and stoichiometry control of γ -Ti₃O₅. Tables 5 shows the X-ray powder diffraction pattern for γ -Ti₃O₅ at 24 °C, of which the refined unit cell dimensions and space group are presented in Table 6 together with those of β -Ti₃O₅² and the high-temperature modification of V₃O₅ (high-V₃O₅).²⁷ By using a Guinier-Hägg focussing camera an optimally exposed powder film was obtained with CuK α ₁ radiation ($\lambda=1.540598$ Å,²⁸ quartz monochromator). A thin Al-foil was used to improve the S/N ratio of the powder film,

which was measured on a SAAB automatic film scanner Mk II.²⁹ The measured powder diffraction pattern of γ -Ti₃O₅ was parabolically corrected³⁰ by five Si ($a=5.431065$ Å²⁸) internal standard lines ($\theta < 40^\circ$).

The figure of merit, F_N , and N_{poss} in Table 5 were defined by Smith and Snyder.³¹ N_{poss} means the number of possible reflexions up to the N th observed reflexion. The powder pattern was indexed by careful comparison of the powder intensities with single crystal diffractometer data. The single crystal data were used to refine the structure³² to a conventional R value of 0.0185 ($R_w=0.0219$) with an overdetermination degree of *ca.* 40 (number of observed independent reflexions/refined parameters 1595/40), $\sigma_{\text{Ti-Ti}}=0.0001-0.0003$ Å, $\sigma_{\text{Ti-O}}=0.0003-0.0005$ Å and $\sigma_{\text{O-O}}=0.0004-0.0009$ Å. The accuracy of the crystal structure determination and of the unit cell refinement ($\sigma(a_i)/a_i=5-6 \times 10^{-5}$,

Table 6. Comparison of the unit cell parameters and space groups of γ -Ti₃O₅, β -Ti₃O₅² and high-V₃O₅.²⁷

	γ -Ti ₃ O ₅ at 24 °C	β -Ti ₃ O ₅ at 20 °C	high-V ₃ O ₅ at 185 °C
<i>a</i> (Å)	9.9701(5)	9.752(1)	9.846(2)
<i>b</i> (Å)	5.0747(3)	3.8020(5)	5.0268(4)
<i>c</i> (Å)	7.1810(4)	9.442(1)	7.009(1)
β (°)	109.867(4)	91.55(1)	109.536(15)
<i>V</i> (Å ³)	341.70	349.95	326.93
Space group	<i>I</i> 2/ <i>c</i> (No. 15)	<i>C</i> 2/ <i>m</i> (No. 12)	<i>I</i> 2/ <i>c</i> (No. 15)

cf. Table 6) also partly demonstrated the quality of the γ -Ti₃O₅ crystals obtained by chemical transport reactions.

Possible deviation from the stoichiometry of the γ -Ti₃O₅ crystals was carefully checked by refining the unit cell parameters for crystals transported with an extreme combination of the empirical values of Q_1 and Q_2 . No changes of the unit cell parameters larger than the measurement errors ($\leq 2\sigma$) were observed even for the γ -Ti₃O₅ crystals which were transported simultaneously with the crystals of Ti₄O₇ or Ti₂O₃. Furthermore, no differences of the unit cell parameters were observed between the vapour transported and non-vapour-transported preparation.⁴

Reports on the crystal structures of γ -Ti₃O₅³² and δ -Ti₃O₅,³³ and of the results of electric conductivity measurements will shortly appear elsewhere.

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