

Synthesis of transparent mixed vanadia/niobia gels and their decomposition to a new metastable $\text{VNb}_9\text{O}_{25}$ phase

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Abstract

Controlled hydrolysis and condensation of a mixture of vanadyl-tris-*n*-propoxide, $\text{VO}(\text{OPr})_3$, and niobium pentaethoxide, $[\text{Nb}(\text{OEt})_5]_2$, at 5°C in propanol yields clear and transparent gels in which the ratio of V:Nb is 1:1, 1:4.5 or 1:9. Oxalic acid and low temperatures are used to slow down the rate of condensation processes. At 800°C , the thermal decomposition of a gel with the composition 1:9 forms a thermodynamically metastable, new phase of the composition $\text{VNb}_9\text{O}_{25}$. At lower temperatures, metastable solid solutions with TT- Nb_2O_5 structure (600°C) and M- Nb_2O_5 structure (700°C) are formed from the amorphous xerogel. The new $\text{VNb}_9\text{O}_{25}$ phase is structurally related to M- Nb_2O_5 . The solid solution with M- Nb_2O_5 structure acts structure directing, leading preferentially to a monoclinic low-temperature form of $\text{VNb}_9\text{O}_{25}$. The full transformation of this metastable phase to the well known tetragonal $\text{VNb}_9\text{O}_{25}$ requires a annealing temperature of about 1000°C .
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1. Introduction

Since the beginning of the nineties, it becomes more and more important to produce complex oxides via so-called “soft chemistry” routes (*chimie douce*) [1]. Here, precursors which are homogeneous as much as possible, are decomposed thermally to the desired crystalline phases. In the best case, homogeneous liquids can be solidified without any phase separation. Reaction limitations of the conventional solid state reaction such as the diffusion are thus avoided and the reaction temperature can normally be lowered. Examples of precursors using this soft chemistry are coprecipitated carboxylates, freeze-dried products, or as in our case, gels.

Intensive research on pure vanadia and niobia gels started around 1985 [2,3]. The evaluated reaction mechanisms [4,5] confirm completely different hydrolysis schemes for vanadium and niobium alkoxides. Monomeric dissolved vanadyl alkoxides hydrolyze completely, forming ribbon-like polyvanadates. Dissolved niobium alkoxides are normally dimeric; they first hydrolyze at the bridging alkoxy groups and then

aggregate to an open polymeric three-dimensional structure [6].

Gelation of mixed components has scarcely been performed, because of the different hydrolysis–condensation conditions. Therefore, mixtures of NbCl_5 and vanadyl alkoxides, which have the disadvantage of chlorine content in the gels, have been mostly used [7–9]. Catauro et al. [10] have prepared amorphous vanadium–niobium mixed oxides with the composition V:Nb of 1:6 by a sol–gel route starting from metal alkoxides. The authors found that the synthesis of transparent, non-opaque gels requires a pre-hydrolysis of the vanadium component and a mixing process of single components at -20°C in presence of HCl. Additionally, the minimum content of niobia is limited to the given composition.

Metal oxides, synthesized through hydrolysis and condensation of metal alkoxides, are generally amorphous. The crystallization of different phases at higher temperatures depends on the precursor. Even small variations of the conditions during the gel preparation as for example the change of the solvent have a large influence [11]. So, as it seems, the composition and preparation of the precursor determines the phase formation.

In this way, Yamaguchi et al. [12,13] have synthesized metastable $\text{V}_4\text{Nb}_{18}\text{O}_{55}$ and VNbO_5 as well as solid solutions of V_2O_5 (up to 10 mol%) in TT- Nb_2O_5 by thermal treatment of pre-

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cipitated alkoxide hydrolysis products. Polte et al. [14] obtained the same compounds by thermal decomposition of freeze-dried alkoxide hydrolysis products. At about 800 °C, $V_4Nb_{18}O_{55}$ and $VNbO_5$ are decomposed forming VNb_9O_{25} and some V_2O_5 . On annealing between 650 and 1000 °C, the single phase solid solution of V_2O_5 (10 mol%) in $TT-Nb_2O_5$ transforms to mixtures of solid solutions with T-, M- and H- Nb_2O_5 structure (and VNb_9O_{25}). However, no single phase compound could be obtained. The transformation of these mixtures to single phase VNb_9O_{25} requires an annealing temperature of about 1050 °C [13,14].

Occurring for the first time, the tetragonal VNb_9O_{25} was synthesized in 1960 by solid state reaction [15]. It is the only known thermodynamically stable phase in the system $V_xNb_{(2-x)}O_5$. Using the mineralizing aid of molten V_2O_5 , tetragonal VNb_9O_{25} can be formed already at about 700 °C [16]. Besides this stable phase and the metastable solid solution with $TT-Nb_2O_5$ structure no further pure phases with the composition of VNb_9O_{25} have been synthesized up to now. Nevertheless, it cannot be excluded that sol–gel synthesis may lead to the formation of further new phases. For their preparation, it seems to be necessary to obtain a gel as homogeneous as possible.

In this paper, clear and transparent gels with the ratio V:Nb=1:1, 1:4.5 and 1:9 were obtained by hydrolysis of vanadyl-tris-propylate and niobium pentaethylate. Chelating agents, which control the reaction rates by modifying the reactivity of the precursors, and a special temperature program prevent spontaneous precipitation and allow the sequential formation of sols and gels. From a so-formed gel of appropriate composition, a metastable bulk vanadium niobium oxide with the composition VNb_9O_{25} has been prepared and characterized by thermal analysis and X-ray powder diffractometry.

2. Experimental

$VO(OPr)_3$ ($Pr = n-C_3H_7$) has been synthesized under moisture-free conditions from V_2O_5 and $PrOH$, distilling off the water with benzene. $[Nb(OEt)_5]_2$ ($Et = C_2H_5$) from H.C. Starck GmbH (Germany) and oxalic acid have been used without further purification. The water content in propanol has been determined (0.23%) and considered for the calculations.

Mixed gel samples with V:Nb=1:1 have been prepared at room temperature in the presence of air using a solution of 0.252 g $H_2C_2O_4 \cdot 2H_2O$ (2 mmol) in 1.5 ml propanol, adding 0.502 ml $[Nb(OEt)_5]_2$ (1 mmol) as starting agent. To this solution 0.470 ml $VO(OPr)_3$ (2 mmol) and subsequently 0.108 ml H_2O (6 mmol) in 1 ml propanol were added. The gel was formed during 1 min. After that, the gel was kept in normal air atmosphere at 5 °C for 12 h, giving a liquid with lower viscosity. At room temperature, this sol reacts to a transparent, brownish gel again, which is stable without any precipitation for about 4 h. Gels containing V:Nb ratios of 1:4.5 and 1:9 were prepared with the same total concentration of metals, adapted ratios of alkoxides and same amounts of water and oxalic acid. Pure vanadia and niobia gels were prepared adding water containing propanol (10% H_2O) to alkoxide solutions of different concentration in propanol, as given in Table 1.

Table 1
Conditions of formation of pure and mixed gels in propanol

Substance	c^a (mol l ⁻¹)	h^b	Additive	t_{gel} (min ⁻¹)
$V(O)(OPr)_3$	1.00	2.6	–	<1
$V(O)(OPr)_3$	0.50	3.1	–	<1
$1/2 [Nb(OEt)_5]_2$	0.71	3.7	–	<1
$V(O)(OPr)_3 + 1/2 [Nb(OEt)_5]_2$	1.06	2.6	Oxalic acid	~1
$V(O)(OPr)_3 + 2.25 [Nb(OEt)_5]_2$	1.06	2.6	Oxalic acid	<1
$V(O)(OPr)_3 + 4.5 [Nb(OEt)_5]_2$	1.06	2.6	Oxalic acid	<1

^a c is the total starting concentration of both alkoxides.

^b h is defined as described in the text.

Xerogel samples were processed by allowing the gel to dry under reduced pressure at 50 °C. After that, it was pre-decomposed for 2 h after increasing the temperature with 2 °C/min to 400 °C. During this annealing process water and alcohol were released, resulting into a hygroscopic, amorphous complex V–Nb-oxide. The following crystallization process was carried out at the given temperature for 4 h in air.

Differential thermoanalysis (DTA) and thermo gravimetric measurements (TG) were performed with a Netzsch STA 409 analyzer. X-ray powder diffraction patterns were collected by a Siemens D5000 diffractometer (Cu $K\alpha$ -radiation; $10^\circ \leq 2\theta \leq 80^\circ$; step scan mode width 0.02°; 1 s per step).

3. Results and discussion

3.1. Gel synthesis

The gelation of pure and mixed alkoxides varies with the hydrolysis ratio and the concentration of the components. Therefore, pure and mixed gels are prepared under different experimental conditions using various mole ratios of $VO(OPr)_3$: $[Nb(OEt)_5]_2$: $PrOH$: H_2O :additive as shown graphically in Figs. 1–3. In Table 1 the results are summarized for characteristic samples. The hydrolysis ratio h is defined as the ratio of moles of water n_{H_2O} to the moles of

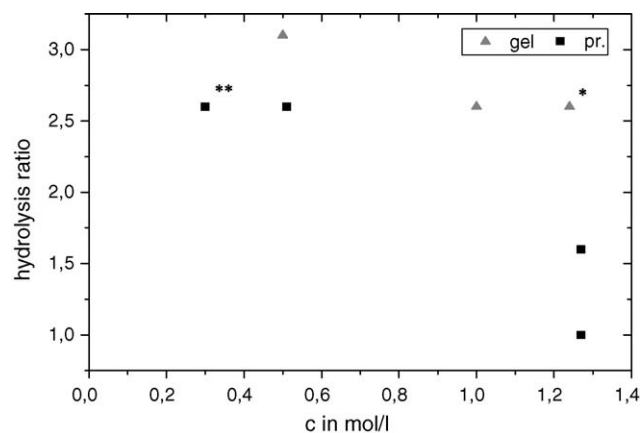


Fig. 1. Hydrolysis of $V(O)(OPr)_3$ in propanol to gels and precipitates (pr.) of V_2O_5 . Additives: (*) 1 mol acetic acid/mol V; (**) 1 mol HNO_3 /mol V. c : starting concentration of vanadyl alkoxide.

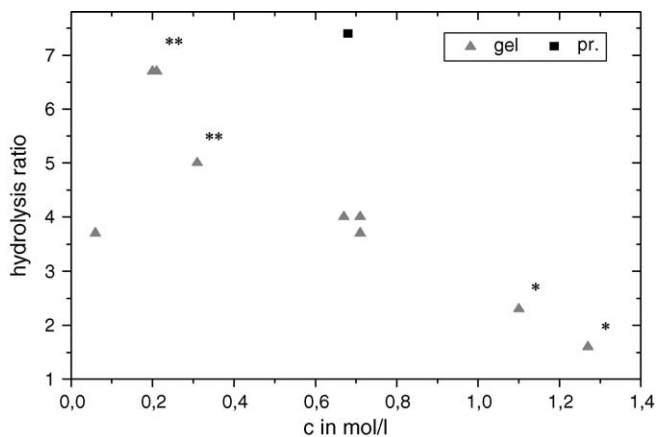


Fig. 2. Hydrolysis of $1/2 [\text{Nb}(\text{OC}_2\text{H}_5)_5]_2$ in propanol to gels and precipitates (pr.) of Nb_2O_5 . Additives: (*) 1 mol acetic acid/mol Nb; (**) HNO_3 in different amounts. c : starting concentration of monomeric niobium alkoxide.

monomeric metal alkoxides ($n(\text{VO}(\text{OPr})_3 + n\text{Nb}(\text{OPr})_5) : h = n\text{H}_2\text{O}/(n(\text{VO}(\text{OPr})_3 + n\text{Nb}(\text{OPr})_5))$).

Pure $\text{VO}(\text{OPr})_3$ can be hydrolyzed and condensed at a hydrolysis ratio $h=2.6$ (Fig. 1). The literature confirms this result indicating that the factor h in 1 M alcoholic vanadium alkoxide solution varies between 3 and 100 [17]. With low amounts of water ($h=3$), an orange gel is obtained. This gel should have other properties as a red gel obtained with $h=100$ or via ion exchange of aqueous vanadate solutions [17].

Niobia gels can be formed with acidic additives. With addition of HCl , the hydrolysis factor h in ethanol was found between 3 [18] and 25 [19]. According to our results, $[\text{Nb}(\text{OEt})_5]_2$ is hydrolyzed and condensed to gels below a hydrolysis ratio of $h=7$ (Fig. 2). The gels often become slightly opaque after 15 min. Gelation to a transparent gel is favoured by HNO_3 or acetic acid as additive. In a very small concentration and hydrolysis ratio field clear niobia gels can be formed without any

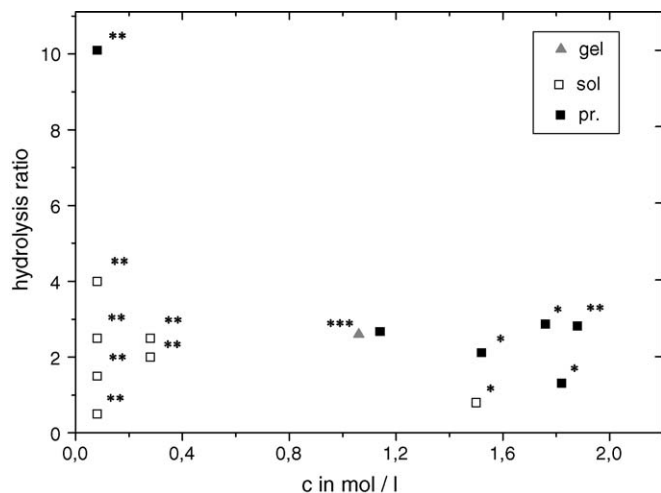


Fig. 3. Hydrolysis of $\text{V}(\text{O})(\text{OPr})_3$ and $1/2 [\text{Nb}(\text{OC}_2\text{H}_5)_5]_2$ in propanol to gels, sols and precipitates (pr.) of V_2O_5 and Nb_2O_5 . Sols are prepared at -10°C . Additives: (*) 1 or 2 mol acetic acid/mol V; (**) 1 mol HNO_3 /mol V; (***) oxalic acid. c : total starting concentration of monomeric alkoxides.

additive. To our knowledge, up to now no clear niobia gel has been prepared without any additives.

The formation of a gel from two metal alkoxides is difficult, if the components hydrolyze and condensate differently. Moreover, the condensation process to small stable oligomers like $\text{Nb}_8\text{O}_6(\text{OEt})_{20}$ has to be suppressed. Thus, a quick hydrolysis connecting a slow condensation is the preferred way.

Dimeric $[\text{Nb}(\text{OPr})_5]_2$ hydrolyzes slower than monomeric $\text{VO}(\text{OPr})_3$ [20]. $[\text{Nb}(\text{OEt})_5]_2$ should react similarly, because of the transesterification process in propanol. During the preparation, $[\text{Nb}(\text{OEt})_5]_2$ is allowed to hydrolyze first. After addition of the vanadium component the condensation process must be slowed down, otherwise a precipitate forms immediately. Therefore oxalic acid is added, chelating probably both transition metals, as found for vanadium alkoxide [21]. Additionally, the condensation rate was reduced by allowing the gel to become equilibrated at low temperature.

The hydrolysis of mixed V- and Nb-alkoxides ($\text{V}:\text{Nb}=1:1$) to sols, gels and precipitates is shown in Fig. 3. Although with and without acidic additives pure $\text{VO}(\text{OPr})_3$ and pure $[\text{Nb}(\text{OEt})_5]_2$ form gels in a similar concentration/hydrolysis ratio field, the application of these conditions to the preparation of mixed gels usually results in a precipitation. Obviously, the hydrolysis–condensation process of one component is strongly influenced by the presence of the other component. Mixed sols can be prepared in a relatively large concentration range, but only below room temperature (-10°C) in acidic solution. Because of the obviously low condensation rate, no gel is formed. At room temperature these sols become unstable and precipitates are formed. Acidic agents, suitable for the synthesis of niobia gels, as HCl , HNO_3 [22,23] or acetic acid cannot prevent the spontaneous precipitation of mixed oxide hydrates.

A transparent gel can only be formed with oxalic acid as chelating agent in a narrow range of alkoxide concentrations. The hydrolysis ratio to form the gel is $h=2.6$, which shows an incomplete exchange of the alkoxide groups. Independently of the $\text{V}:\text{Nb}$ ratio, the gels turn in opaque gels during 15 min because of a rapid condensation process. Therefore, clear gels obtained after mixing the components at room temperature, were aged at lower temperature (5°C). After 12 h of aging, the gels stay clear at room temperature for 4 h and can be dried and annealed.

3.2. Pyrolysis of gels and phase formation

A dried xerogel of the composition $\text{V}:\text{Nb}=1:9$ was heated at various temperatures for 4 h. Fig. 4 shows the obtained X-ray powder diffraction patterns. At 600°C , a crystalline solid solution with the composition nine $\text{Nb}_2\text{O}_5 \cdot \text{V}_2\text{O}_5$ in the pseudo hexagonal TT-modification of Nb_2O_5 (also called $\delta\text{-Nb}_2\text{O}_5$) is formed. At 700°C , a tetragonal $\text{M-Nb}_2\text{O}_5$ ($\beta\text{-Nb}_2\text{O}_5$) or a solid solution of V_2O_5 in this phase is the main product. The excess of V_2O_5 forms $\text{V}_4\text{Nb}_{18}\text{O}_{55}$, a thermodynamically metastable $(\text{V}, \text{Nb})_2\text{O}_5$ phase. Heating the xerogel between 800 and 900°C , the result obtained reveals a new, unknown phase beside some traces of unreacted $\text{M-Nb}_2\text{O}_5$. The composition should be

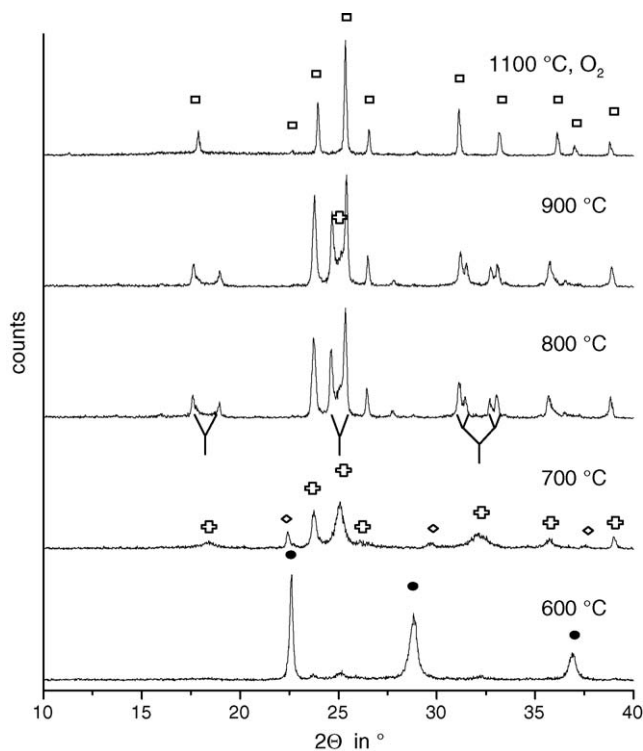


Fig. 4. X-ray powder diffraction patterns of a gel in the composition V:Nb = 1:9 after annealing in air at different temperatures. TT-Nb₂O₅ (●), M-Nb₂O₅ (+), V₄Nb₁₈O₅₅ (◊), high temperature VNb₉O₂₅ (□). Metastable VNb₉O₂₅ is not marked.

VNb₉O₂₅, since no other phases are detectable by XRD. The new phase can be regarded as a low temperature modification of VNb₉O₂₅ (see below). The well known, thermodynamically stable high-temperature form of VNb₉O₂₅ with a tetragonal block structure [24] forms on annealing at 1100 °C. Here, an oxygen atmosphere is necessary to yield a slightly yellow product and to avoid partial reduction, since the substance generally has a high oxygen partial pressure. As function of the temperature and the surrounding oxygen partial pressure, a reversible release of oxygen can be observed [20]. The compound can therefore be used excellently as an oxidative catalyst. That will be the scope of another paper.

To give an overview of the phase formation, a thermal analysis of the precursor after heating it at 400 °C has been made. DTA and TG curves are shown in Fig. 5. Up to 530 °C a small amount of water is released because of the hygroscopic nature of the pre-treated sample. The exothermic peak between 530 and 670 °C in the DTA curve is usually connected to the burn-out of traces of carbon [14,20], which stems from the chemically bonded alcohol groups. This carbon is firmly bonded, much more than expected, and a further small decrease of mass can be noticed up to 1400 °C. Because of the obviously low rate of transformation between the different phases the DTA curve does not reveal clear informations concerning phase transitions.

The alkoxide-derived carbon is often found to induce the formation of a metastable phase instead of the expected thermodynamically stable phase. It can be therefore explained that, instead of VNb₉O₂₅, the metastable phases with TT- and M-

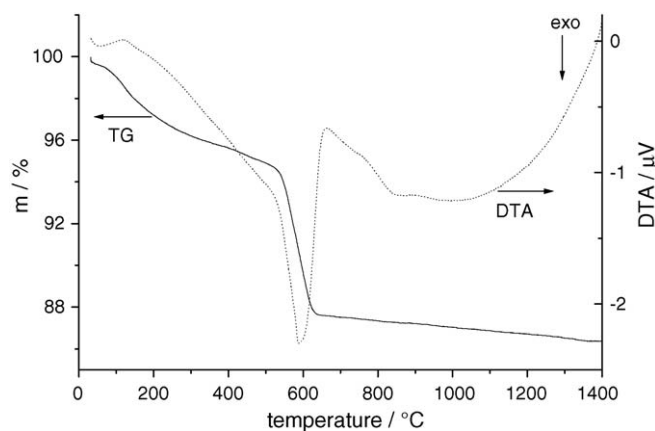


Fig. 5. DTA/TG of a gel of the composition V:Nb = 1:9, pretreated at 400 °C. Heating rate: 10 K/min, atmosphere: air.

Nb₂O₅ structure are formed at first. At 700 °C, the occurrence of traces of V₄Nb₁₈O₅₅ beside the solid solution with M-Nb₂O₅ structure shows that the solubility V₂O₅ in M-Nb₂O₅ is lower than in TT-Nb₂O₅. At 800 °C, the M-Nb₂O₅ solid solution and V₄Nb₁₈O₅₅ react to the new metastable low-temperature VNb₉O₂₅ phase (lt-VNb₉O₂₅). In Fig. 4, connection lines show the possible relationship between the powder pattern of M-Nb₂O₅ and the X-ray pattern of the new phase. A single or double splitting of the peaks is found, which indicates structural relatedness between both phases and a lowering of symmetry during the phase transformation. A comparison with patterns of H-Nb₂O₅ (α-Nb₂O₅) and thermodynamically stable high-temperature VNb₉O₂₅, as shown in Fig. 6, confirms the formation of a new phase. Structural relationships between both VNb₉O₂₅ phases are also pointed out.

Another experiment confirms the essential role of M-Nb₂O₅ forming lt-VNb₉O₂₅. Annealing a nearly carbon free mixture 9:1 of reactive TT-Nb₂O₅ and V₂O₅ in oxygen-reduced atmosphere (argon with 10⁻⁴ bar oxygen) at 800, 900 or 1000 °C leads to a M-Nb₂O₅ phase. Some traces of V₄Nb₁₈O₅₅ are only found after annealing at 800 °C. A controlled reducing atmosphere therefore acts as a stabilizer on the M-Nb₂O₅ phase. This is confirmed by the fact that the M-Nb₂O₅ sample, formed in a reducing atmosphere, is also transformed to the new lt-VNb₉O₂₅ by an annealing process at 800 °C in the presence of air atmosphere. The following scheme summarizes the phase formation processes described above:

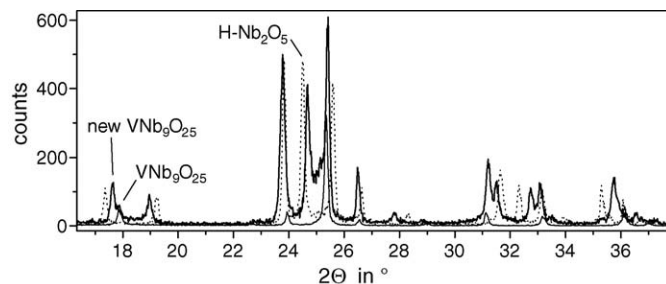
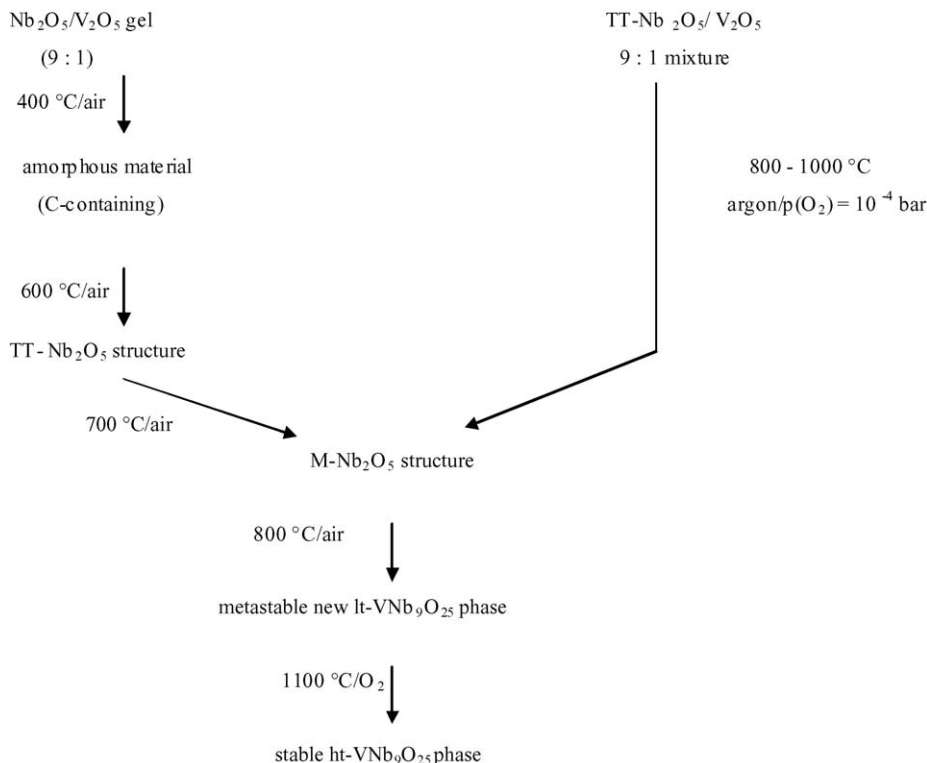


Fig. 6. Overlay of X-ray powder diffraction patterns of H-Nb₂O₅, ht-VNb₉O₂₅ and lt-VNb₉O₂₅.



The X-ray powder pattern of the metastable lt-VNb₉O₂₅ phase is very similar to that of WNb₁₂O₃₃ described by Roth and Wadsley (PDF 44–465). The structure of WNb₁₂O₃₃ consists of 3 × 4 × 4 blocks of NbO₆ octahedrons, which are joined by sharing edges, and with tetrahedrally coordinated W atoms ordered at the junctions of every four blocks. The unit cell parameters are $a = 22.37$, $b = 3.825$, $c = 17.87$ Å, $\beta = 123.6^\circ$, space group C2 [25]. All the peaks of the X-ray powder pattern of lt-VNb₉O₂₅ can also be indexed in the monoclinic crystal system. The (hkl)-values are given in the upper part of Fig. 7. The unit cell parameters ($a = 22.22$, $b = 3.839$, $c = 17.75$ Å, $\beta = 123.3^\circ$) are very similar to these of WNb₁₂O₃₃. Using these cell parameters and the metal atomic parameters (x , y , z) given in [25] for WNb₁₂O₃₃,

a X-ray powder diffractogram for a hypothetical compound V(Nb_{11.7}V_{0.3})O_{32.5} of the composition VNb₉O₂₅ was calculated. The result is shown in the lower part of Fig. 7. The high degree of agreement between the experimental powder diffractogram of lt-VNb₉O₂₅ and the calculated diffractogram speaks for the existence of a solid solution phase V(Nb_{12-x}V_x)O_{32.5} with $x = 0.3$ and WNb₁₂O₃₃-structure. The solid solution phase contains some vanadium on niobium sites and vacancies in the oxygen sublattice.

The crystallization of the lt-VNb₉O₂₅ phase with the structure of WNb₁₂O₃₃ should be a kinetically controlled process and can be explained as follows: M-Nb₂O₅ as a necessary precursor phase crystallizes with an irregular block structure. First of all, a tetragonal structure with 4 × 4 blocks of NbO₆ octahedrons (space group $I4/mmm$) was suggested [27]. Afterwards, it was shown by TEM that the XRD pattern with a relatively small number of broad peaks is the result of an averaging of different block sizes and block connections [28]. On annealing the M-(Nb, V)₂O₅ phase in air atmosphere a rearrangement of the irregular block structure takes place in which the already existing 3 × 4 blocks act as crystallization centers. This process results in the transformation into lt-VNb₉O₂₅ with a regular 3 × 4 block structure. Only above a temperature of 900 °C the further transformation into the thermodynamically stable VNb₉O₂₅ phase takes place.

Thermodynamically stable VNb₉O₂₅ formed in oxygen atmosphere has a slightly yellow colour and shows thermochromism, as all mixed phases in the system V₂O₅/Nb₂O₅. At 1100 °C in air atmosphere VNb₉O₂₅ loses some oxygen. This leads to the formation of a substoichiometric brown substance, designated in literature [24] as VNb₉O_{24.9}. Thus we obtained for the first time the pale yellow non-reduced phase.

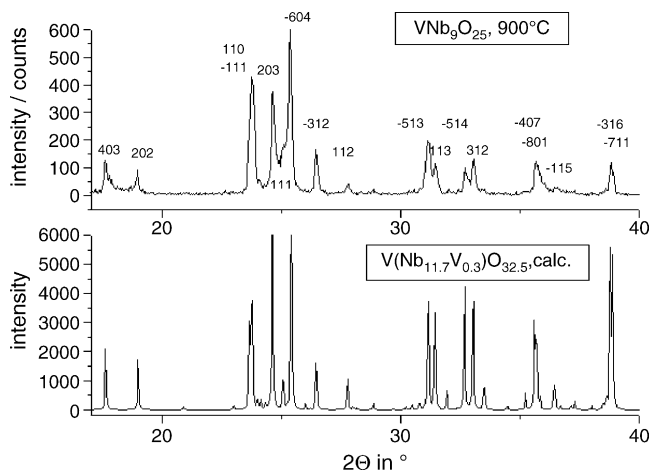


Fig. 7. X-ray powder diffraction pattern of lt-VNb₉O₂₅ (upper part) and calculated powder diffraction pattern of V(Nb_{11.7}V_{0.3})O_{32.5} using a Powder Cell program [26] (lower part).

4. Conclusion

Vanadium and niobium alkoxides can be used as precursors to get transparent, homogeneous (V,Nb)₂O₅ gels. Different hydrolysis and condensation rates can be equalized by controlling the hydrolysis, condensation process with chelating agents and a special temperature regime. Because of the high homogeneity, these gels are good candidates for the preparation of new, metastable phases in the system V₂O₅/Nb₂O₅. This was shown for the synthesis of a new It-VNb₉O₂₅ phase via an M-Nb₂O₅ phase. Obviously, the formation of a nearly single phase product with M-Nb₂O₅ structure is induced by a “reducing agent” within the precursor (unburned carbon). The M-Nb₂O₅ phase transforms preferentially to the new low-temperature It-VNb₉O₂₅ phase with a 4 × 3 × 4 block structure. Its transformation to the well known thermodynamically stable tetragonal form with a 3 × 3 × 4 block structure requires an annealing process at about 1100 °C.

This result differs from results of Amountza et al. [29] who obtained tetragonal VNb₉O₂₅ by a controlled hydrolysis of VO(OC₂H₅)₃/Nb(OC₂H₅)₅ mixtures without additives and their annealing at only 680 °C for 100 h. Possibly, some molten V₂O₅ is formed intermediately from the slightly inhomogeneous precursor, which acts as mineralizing aid. The X-ray powder diffractogram shown in [29] gives some signs for this assumption.

It can be concluded that the variation of the carbon content, the composition of a sol gel precursor and the variation of the reaction atmosphere change the nature of intermediate phases. Therefore, these take control of the out coming products. In this context, the large variety of modifications of Nb₂O₅ plays an important role, because they can “direct” the phase formation and the structure of complex oxide phases formed in the system V₂O₅/Nb₂O₅. More of this structure directing effect will be the scope of another paper.

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