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$VNb_9O_{25-\delta}$—Synthesis, electrical conducting behaviour and density functional theory (DFT) calculation

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ABSTRACT

In order to investigate the influence of the oxygen partial pressure ($p(O_2)$) on the electrical conductivity, VNb_9O_{25} was prepared by thermal decomposition of freeze-dried oxalate precursors and by a solid state reaction of V_2O_5/Nb_2O_5 mixtures. The samples were characterised by X-ray diffraction, grain size analysis and scanning electron microscopy (SEM). The electrical conductivity of the *n*-type semiconductor $VNb_9O_{25-\delta}$ can be interpreted as an activated hopping process with a preferred localisation of charge carriers at V(IV) centres. The electronic structure of $VNb_9O_{25-\delta}$ was calculated within the framework of the local density approximation (LDA) to DFT. Partial reduction of V(V) centres causes localised vanadium states to appear inside the band gap. The calculated activation energy values are in good agreement with the experimental ones.

1. Introduction

Vanadium and niobium oxides are well investigated with emphasis on its catalysis and electrochemical applications [1–3]. Mixed oxides of the quasi-binary system V_2O_5–Nb_2O_5 promise catalytic selectivity [4,5] due to the partially reducible V_2O_5 embedded into the hardly reducible but selective Nb_2O_5 [5,6]. Examples of catalytic reactions are the selective oxidation of propane to acrolein over supported V_2O_5/Nb_2O_5 catalysts [4] and the propane oxidative dehydrogenation reaction to propene catalysed by V_2O_5/Nb_2O_5 mixed metal oxides and supported metal oxides [5,7,8].

VNb_9O_{25} is the only known thermodynamically stable phase of the quasi-binary system V_2O_5–Nb_2O_5 [9]. It was synthesised for the first time in 1960 by a solid state reaction (SSR) [10]. Its structure was determined by consideration of isostructural compounds [11], such as PNb_9O_{25} [12], and later refined by single crystal data analysis [13]. The structure of VNb_9O_{25} consists of 3×3 blocks of $[NbO_6]$-octahedra linked by corner-sharing $[VO_4]$ tedrahedra. A low temperature modification, which is obtained via sol–gel synthesis at 600 °C, is known to be a solid solution of 10% V_2O_5 in TT–Nb_2O_5, the low ("tief") temperature modification of Nb_2O_5 [14]. The transformation TT→VNb_9O_{25} is irreversible suggesting that this TT modification is metastable. Recently, we were able to synthesise a further metastable VNb_9O_{25} phase via a special sol–gel process from alkoxides [15].

Besides VNb_9O_{25} there are two further phases known in the quasi-binary system V_2O_5–Nb_2O_5 with the compositions $V_2Nb_9O_{27,5}$ [14] and $VNbO_5$ [16]. Both are metastable and can be synthesised via precursor decomposition at low temperatures between 500 and 700 °C. Their decomposition into VNb_9O_{25} and V_2O_5 starts above 750 °C [14,16]. It was shown recently that all the hitherto known phases in the V_2O_5–Nb_2O_5 system can be synthesised in a relatively simple manner by thermal decomposition of freeze-dried solutions of ammonium oxo-oxalato-niobate and ammonium vanadate [17].

The phase formation process conducted at low temperatures modifies the sample morphology compared to a sintered sample of equal composition. This pertains not only to a varying particle size distribution, but also to altered grain boundary properties. Both features are thought to influence the electrical characteristics of VNb_9O_{25} after synthesis via a soft-chemistry route (SCR) [18]. Although the conductivity mechanisms of V_2O_5 and Nb_2O_5 as well as their oxygen partial pressure ($p(O_2)$) dependency are well investigated [1,3,19], details on the electrical behaviour of VNb_9O_{25} are not reported thus far.

To investigate the influence of $p(O_2)$ on the electrical conductivity, VNb_9O_{25} was prepared via decomposition of a freeze-dried mixture of oxo-oxalato-niobate(V) and oxo-oxalato-vanadate(IV). In addition, a solid state reaction was used to synthesise VNb_9O_{25} in order to compare the dependence of physical and chemical properties on the synthetic pathway.

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Conductivity measurements were performed along with temperature-dependent oxygen-loss measurements in a temperature range from 300 to 800 °C. From these measurements the activation energy was determined and compared with DFT-LDA electronic structure calculations.

2. Experimental

2.1. Sample preparation

Unconventional synthesis of VNb_9O_{25} was performed via the freeze-drying method. Aqueous solutions of oxo-oxalato-vanadate(IV) (V_2O_5 in oxalic acid, molar ratio $V^{5+}:C_2O_4^{2-} = 1:2.5$) and oxo-oxalato-niobate(V) (amorphous Nb_2O_5 in oxalic acid, molar ratio $Nb^{5+}:C_2O_4^{2-} = 1:3$) of composition V:Nb = 1:9 (pH = 1.5) were frozen to liquid nitrogen temperature. The frozen mixture was dried in a vacuum chamber of an Alpha 2-4 freeze-drying apparatus (Christ) at a pressure of 0.020–0.040 mbar from −33 to 17 °C. The resulting water-soluble powder was pre-decomposed by heating at a rate of 5 K/min up to 350 °C, and keeping it for 30 min at this temperature. The subsequent phase formation was carried out for 5 h at a temperature of 1000 °C.

To assess whether any oxalic acid might get lost during the freeze-drying process (see Section 3.1), the behaviour of free oxalic acid under vacuum atmosphere was studied as well. To this end, a 0.1 M oxalic acid was freeze-dried using similar conditions as described above.

The thermal decomposition of niobium-free oxo-oxalato-vanadate(IV) and vanadium-free oxo-oxalato-niobate(V) was investigated with respect to potentially cumulative effects.

In order to prepare VNb_9O_{25} by solid state reaction, a mixture of vanadium and niobium oxide V_2O_5:Nb_2O_5 = 1:9 was annealed for 24 h at 1000 °C on air. Two different species Nb_2O_5 were used: a freshly precipitated amorphous Nb_2O_5 and its high temperature H modification.

2.2. Sample characterisation

The content of oxalic acid and of the vanadium(IV) species within the freeze-dried product was determined by manganometric titration. Oxo-oxalato-vanadate(IV)–oxo-oxalato-niobate(V) mixtures were dissolved in 5% sulphuric acid. After heating the solutions for 10 min in the presence of Na_2SO_3, they were titrated with 0.02 M $KMnO_4$ solution.

Differential thermal analysis (DTA) and thermogravimetry (TG) were performed by means of a Netzsch STA 409 PC-Luxx analyser coupled with a quadrupole mass spectrometer QMG 420 (Balzers).

X-ray powder diffraction was carried out on a Siemens D5000 X-ray diffractometer using Cu$K\alpha_1/K\alpha_2$-radiation. Data were collected for 1 h within a $20^\circ \leq 2\theta \leq 80^\circ$ range.

For the determination of the particle size distribution by dynamic light scattering (DLS) a particle size analysator LS230 (Beckmann Coulter) was utilised. The three-cycle measurements (5 min) of the samples dispersed in a 0.1% $Na_4P_2O_7$ solution were carried out after a 5 min supersonic pre-treatment.

The specific surface measurements were conducted by the Brunauer–Emmett–Teller method (BET) with nitrogen (device calibration with helium gas) using a SA 3100 apparatus (Beckmann Coulter).

IR absorption spectra were measured on a BioRad Excalibur FTS 3000.

Scanning electron microscopy (SEM) was performed on a Philips XL30 apparatus, using a LaB_6-cathode and an acceleration voltage of 25 kV.

The temperature-dependent oxygen loss ($p(O_2)$ measurement) was controlled in a tube furnace with oxygen-sensitive sensors at each port. Samples were heated in steps of 100 K up to 1000 °C while an inert gas flow (nitrogen with $p(O_2) = 20$ Pa or argon with $p(O_2) = 620$ Pa) was maintained. After each step the system was allowed to thermally equilibrate before resuming the heating programme [20].

The electrical conductivity was measured using the direct current (DC) four-point method. Therefore two current and two potential platinum leads were sintered into a pill of VNb_9O_{25} for 5 h at 950 °C in oxygen atmosphere. The density of the ceramic pill of the SCR sample is $d = 2.517\,g/cm^3$ (porosity 44.8%); the density of the SSR ceramic sample is $d = 2.754\,g/cm^3$ (porosity 39.6%). Before evaluation, the conductivity results were corrected for sample porosity as given in [21].

Heating and cooling processes were carried out with rates of 6 K/min and the maximum temperature of 800 °C was held for 1 h. All measurement cycles were repeated at least twice under the same experimental conditions before the $p(O_2)$ was changed. To investigate the adjustment to equilibration at 800 °C, an additional measurement in air with a dwell time of 5 h was included.

3. Results and discussion

3.1. Decomposition of the freeze-dried samples

As for trisammonium-oxo-trisoxalato-niobate [22], the decomposition of freeze-dried ammonium-free oxo-oxalato-vanadate(IV), oxo-oxalato-niobate(V) and of their mixtures takes place in three major steps: (I) vaporisation of crystal water between 85 and 130 °C; (II) decomposition of oxalate by a quick release of CO, CO_2 and chemically bound H_2O from 140 to 200 °C; and (III) a slow release of CO and CO_2 from 200 to 330 °C (350 °C for oxo-oxalato-vanadate(IV)). This is evidenced by the mass spectroscopic analysis of the gaseous decomposition products. The mass loss of 3–5% at temperatures between 350 and 1000 °C in argon, and at about 600 °C in air, displays the low remaining carbon concentration of the pre-decomposed powders of Nb_2O_5 and VNb_9O_{25} after heating in air (Fig. 1, Table 1). All in all, a heating process in air results in compounds with stable compositions above 600 °C, while a treatment in argon leads to a higher mass loss in case of V_2O_5 (which is reduced to V_2O_{3+x}), and to a reduced mass loss for Nb_2O_5 and VNb_9O_{25} because of the higher residual carbon concentrations.

The freeze-dried powders of the oxo-oxalato-metallates are hygroscopic. This can be observed by an increasing agglomeration and discolouring of the samples after storage in ambient air. The content of crystal water strongly depends on the dwell time and the conditions during the freeze-drying process as well as on the sample storage. A freshly prepared sample of the 1:9 mixture contains less water than a few weeks old sample (Table 1). An analysis of the remaining compounds after the heating process in air coupled with the results of the manganometric titration is presented in Table 1. Surprisingly, the averaged ratio between metal atoms and oxalate ions for the 1:9 mixture is 1:2.3 instead of 1:2.9, as expected from the composition of the precursor solution. The loss of oxalate probably results from oxalic acid in the initial precursor solution according to equilibrium (1) [23]:

$$H_3NbO(C_2O_4)_3 + 2H_2O \rightleftarrows H_2NbO(OH)(C_2O_4)2H_2O + H_2C_2O_4 \qquad (1)$$

Oxalic acid completely sublimates under the chosen freeze-drying conditions within 30 h [24].