JOURNAL OF SOLID STATE CHEMISTRY **116**, 369–377 (1995)

On the Nonstoichiometry in Rutile-Type $\approx$SbVO$_4$

Angel Landa-Cánovas,*,† Jerker Nilsson,‡ Staffan Hansen,*,†,[1] Kenny Ståhl,† and Arne Andersson‡

*National Center for HREM, †Inorganic Chemistry 2, ‡Chemical Technology, Chemical Center, University of Lund,
P.O. Box 124, S-221 00 Lund, Sweden

Received September 19, 1994; in revised form November 4, 1994; accepted November 11, 1994

Heating equimolar mixtures of Sb_2O_3 and V_2O_5 at 800°C in flowing gas with varying O_2/N_2 ratios produces a continuous nonstoichiometric series of rutile type, i.e., $Sb_{0.9}V_{0.9+x}\square_{0.2-x}O_4$, $0 < x < 0.2$, and varying amounts of α-Sb_2O_4. Oxidized $Sb_{0.9}V_{0.9}\square_{0.2}O_4$, $a = 4.63$, $c = 3.03$ Å (X ray powder data, XRD), is formed in pure oxygen and exhibits a modulated structure with an approximate supercell: $2\sqrt{2}a, 2\sqrt{2}b, 4c$ (electron diffraction, ED). In pure nitrogen, reduced $Sb_{0.9}V_{1.1}O_4$, $a = 4.60$, $c = 3.08$ Å (XRD), with the supercell $\sqrt{2}a$, $\sqrt{2}b$, $2c$ (ED), is produced. Heating at intermediate partial pressures of oxygen give phases with the basic rutile cell $a = b$, c (XRD, ED). The formulation of this series is supported by data obtained by Fourier transform infrared spectroscopy. Under reducing conditions (in pure nitrogen), a solid solution series of $Sb_{0.9}V_{1.1}O_4$ and VO_2 is observed, i.e., $Sb_{0.9-y}V_{1.1+y}O_4$, $0 < y < 0.7$. Vanadium-rich $Sb_{0.2}V_{1.8}O_4$, with $a = 4.56$, $c = 2.99$ Å (XRD), exhibits a basic rutile lattice with diffuse intensity between Bragg spots (ED).

1. INTRODUCTION

Although rutile-type $M_{1+x}O_2$ materials, where the cation excess is accommodated by a crystallographic shear mechanism (1), are well characterized, cation-deficient rutiles have indeed received much less attention. One cation-deficient rutile is $\approx$SbVO$_4$, which plays a key role in a recently developed catalyst for the direct production of acrylonitrile by ammoxidation of propane (2–4). It has been shown that an excess of α-Sb_2O_4 (orthorhombic) improves the selectivity for acrylonitrile formation (5–7), although the reasons for this behavior are not yet fully clarified. The major process used world-wide for the production of acrylonitrile is the SOHIO/BP process, converting propylene feedstock. However, considering the substantial price difference between propylene and propane, which is on the order 10 U.S. cents/lb, a process using propane feedstock is obviously an interesting alternative (3).

Birchall and Sleight (8) showed by Mössbauer spectroscopy that Sb is in oxidation state 5+ in $\approx$SbVO$_4$. They reported two different phases at 800°C: an oxidized $Sb_{1-x}V_{1-x}O_4$ phase, with the composition $Sb_{0.92}V_{0.92}O_4$ when prepared in air, and a reduced $Sb_{1-y}V_{1+y}O_4$ phase with an estimated composition of $Sb_{0.95}V_{1.05}O_4$, when prepared in a closed tube. Later, Berry *et al.* (9) reported two different reduced phases: one prepared in a closed tube or in flowing commercial nitrogen, with the composition $Sb_{1-y}VO_{4-2y}$ $(0 < y < 0.1)$ and a second with the composition $Sb_{1-y}VO_{4-1.5y}$ $(0 < y < 0.1)$ when prepared in flowing, oxygen-free, nitrogen. It is worthwhile noting that at maximum degree of reduction, these two phases have compositions corresponding to $Sb_{0.95}V_{1.05}O_4$ and $Sb_{0.94}V_{1.04}O_4$, respectively. The stoichiometric composition SbVO$_4$ was not observed (8, 9), although the chemical formulas were all written with SbVO$_4$ as a formal end member.

Recently, Hansen *et al.* (10) studied the crystal structure of an $\approx$SbVO$_4$ rutile, which was prepared in air, by neutron and X ray powder diffraction. The product was shown to be a cation-deficient $Sb_{0.92}V_{0.92}O_4$ phase and the present investigation was undertaken in order to clarify the bulk redox-behavior of $\approx$SbVO$_4$, where basic knowledge is needed to understand the more complex redox reactions occurring at the crystal surfaces during catalysis. In this context, preparing $\approx$SbVO$_4$ in an open system with flowing gas is the most relevant approach. The present paper concentrates on the crystal chemistry of $\approx$SbVO$_4$, while crystallographic data and structural considerations will be reported later.

2. EXPERIMENTAL

Synthesis

Two different series of Sb–V–O samples were prepared. For the first series, hereafter the *equimolar series* or *1 : 1 series* for short, equimolar mixtures of V_2O_5 (Riedel-de Haën, 99.5%) and Sb_2O_3 (Merck, >99%) were mixed and then heated in a silica ship (placed in a silica tube) under flowing gas with varying partial pressures of oxygen (0–1 atm). The mixtures were heated at a rate of 10°C min^{-1} to 800°C, then held at this temperature for 17 hr, and finally quenched to room temperature, all under

---

[1] To whom correspondence should be addressed.

0022-4596/95 $6.00

the appropriate atmosphere. The second series, hereafter the *reduced series*, was prepared with different V_2O_5/Sb_2O_3 molar ratios, from 1 : 1 to 10 : 1, in an oxygen-free flow of nitrogen at 800°C for 17 hr. Oxygen (Aga, >99.5% O_2) and nitrogen (Aga Plus, <5 ppm O_2 and <5 ppm H_2O) were mixed using Hi-Tec mass flow controllers. Oxygen-free nitrogen was prepared by passing commercial nitrogen through a several-centimeters-long skein of thin copper wire, which was placed just in front of the ship in the furnace. By the end of each experiment, fresh Cu metal always remained closest to the ship, and we assume that the oxygen pressure was below the equilibrium pressure over a Cu/Cu_2O mixture, which is on the order of 10^{-11} atm at the present temperature.

Characterization

All samples were studied by X ray powder diffraction using a Guinier-Hägg camera with $CuK\alpha_1$ radiation (wave length 1.54056 Å) and with Si (a = 5.43088 Å) as an internal standard. X ray intensity data for endmembers of the 1 : 1 series were collected in reflection mode on a Huber single-crystal diffractometer with a spinning powder holder and $MoK\alpha$ radiation. Representative samples were examined in a transmission electron microscope (JEOL 2000FX) at 200 kV and energy-dispersive X ray microanalysis (EDX) was carried out with a LINK AN10000 system and a typical spot size of 50 nm. For quantification, a $Sb_{0.92}V_{0.92}O_4$ sample prepared in air and characterized in our previous work (10) was used as a standard with V : Sb = 1.

Density measurements were made in a Micromeritics gas-pycnometer Accupyc 1330, measuring the pressure change of helium at room temperature in a calibrated volume. Before the density measurement, all samples were first heated at 140°C for 1 hr and were then allowed to cool to room temperature in a desiccator. Thermogravimetry (TGA) was performed using a Cahn apparatus, System 113. The sample was heated to 800°C in 1 hr, kept at this temperature for 2 hr and then allowed to cool to room temperature in 3 hr, all in the appropriate atmosphere. The weight was measured before and after the heating cycle. Fourier transform infrared transmission spectra were recorded on a Nicolet 20 SXC spectrometer equipped with a CsI beamsplitter, allowing recordings down to 200 cm^{-1}. Disks containing 3 mg of sample and 200 mg of KBr were pressed. Spectra were recorded at room temperature in an atmosphere of dry air. The resolution was 2 cm^{-1} and 1000 scans were averaged.

3. RESULTS

3.1. X Ray Diffraction

Equimolar series. Table 1 shows the phases present and the unit cell parameters of $\approx SbVO_4$ in the 1 : 1 series of samples, as determined from Guinier powder diffraction data. The X ray intensities show that when the partial pressure of O_2 ($P(O_2)$) decreases, the amount of α-Sb_2O_4 increases. No α-Sb_2O_4 is observed when oxygen partial pressures equal to or higher than 0.10 atm are used. The oxidized endmember thus exhibits a V : Sb ratio close to one, while the reduced endmember of this series is more rich in vanadium. Only reflections corresponding to a basic rutile unit cell were observed in the powder X ray patterns after exclusion of any α-Sb_2O_4 or V_2O_5 reflections, except in the oxidized samples prepared in pure oxygen, which presented three weak additional peaks that could not be indexed as rutile.

TABLE 1

X Ray Powder Diffraction[a] of Nonstoichiometric $SbVO_4$ Prepared from Equimolar Mixtures of Sb_2O_3 and V_2O_5 Heated at 800°C in Flowing Gas with Varying O_2/N_2 Partial Pressures

		Lattice parameters	
$P(O_2)$/atm	Crystalline phases	a/Å	c/Å
1.00	$\approx SbVO_4$, trace V_2O_5	4.6304(5)	3.0330(6)
0.21	$\approx SbVO_4$	4.6222(3)	3.0392(3)
0.10	$\approx SbVO_4$	4.6212(4)	3.0440(4)
0.05	$\approx SbVO_4$, α-Sb_2O_4[b]	4.6148(4)	3.0547(4)
0.03	$\approx SbVO_4$, α-Sb_2O_4	4.6112(5)	3.0623(5)
0.01	$\approx SbVO_4$, α-Sb_2O_4	4.6059(5)	3.0765(5)
0.00[c]	$\approx SbVO_4$, α-Sb_2O_4	4.5999(5)	3.0832(5)

[a] Guinier-Hägg data.

[b] The X ray intensities show an increasing amount of α-Sb_2O_4 with decreasing $P(O_2)$.

[c] Nitrogen purified over Cu wire at 800°C, $<10^{-11}$ atm oxygen.

In Fig. 1 the variation of unit cell parameters c vs a is

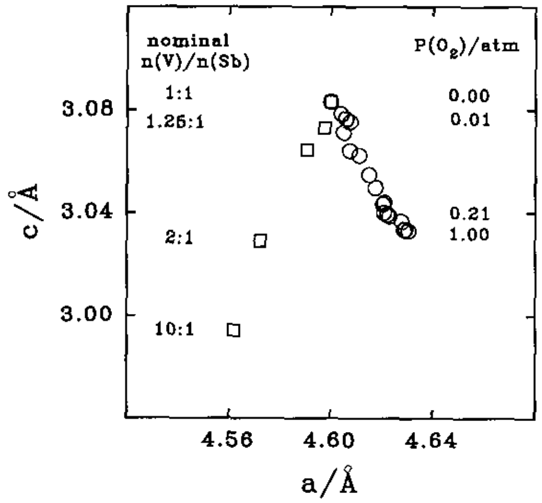

FIG. 1. Tetragonal unit cell parameters for $\approx SbVO_4$. First series (circles) prepared from equimolar V_2O_5/Sb_2O_3 mixtures at different oxygen partial pressures $P(O_2)$. Second series (squares) prepared in reducing atmosphere with $P(O_2) < 10^{-11}$ atm and varying nominal atomic ratios of V : Sb in the oxide mixture.

plotted (for both series). According to Fig. 1 the first series of synthesis with V : Sb nominally equal to one contains a continuous series of rutile-type materials, where the unit cell parameters varies with the partial pressure of oxygen in the synthesis atmosphere.

The existence of a continuous series of materials as a function of oxidation level was also directly tested in a separate experiment. First an oxidized phase was prepared by heating a 1 : 1 oxide mixture in pure oxygen. This oxidized phase was then subjected to consecutive heat treatments in flowing gas, with a decrease in $P(O_2)$ between each heating. Powder patterns, recorded after each heat treatment, showed a rutile-type ≈SbVO$_4$ with lattice parameters changing in a way similar to that of the previous series in Table 1. Thus, the ≈SbVO$_4$ phase became more reduced after each run with a lower oxygen partial pressure in the furnace.

Reduced series. In the reduced series, where the nominal V : Sb ratio was varied, all samples except the most V-rich member with V : Sb = 10 : 1 were monophasic and exhibited only the basic rutile-type X ray diffraction maxima. This series of synthesis also seems to present a continuous series of rutiles and the unit cell parameters in this case depend on the vanadium content; cf. Fig. 1. The sharp kink where the two series meet (at the top of the diagram) indicates that the solid state mechanisms accommodating the compositional change, are different in the two series of rutiles.

3.2. *Electron Diffraction and Imaging*

Crystal shape. Imaging and diffraction in the electron microscope show that the samples in the first (1 : 1) series contain micrometer-sized ≈SbVO$_4$ crystals, with typical rutile (TiO$_2$) crystal habit and sharp edges, as well as larger (10–50 micrometers) α-Sb$_2$O$_4$ crystals of badly defined shape. Larger, millimeter-sized ≈SbVO$_4$ crystals were only observed in vanadium-rich samples of the reduced series, where crystallization occurred from the melt.

Equimolar series. Selected area electron diffraction patterns of representative ≈SbVO$_4$ crystals from the 1 : 1 series are shown in Fig. 2. These selected area diffraction patterns were taken from crystals oriented along the [101] rutile direction, which proved to be the most sensitive to the weak satellite reflections or diffuse intensities ob-

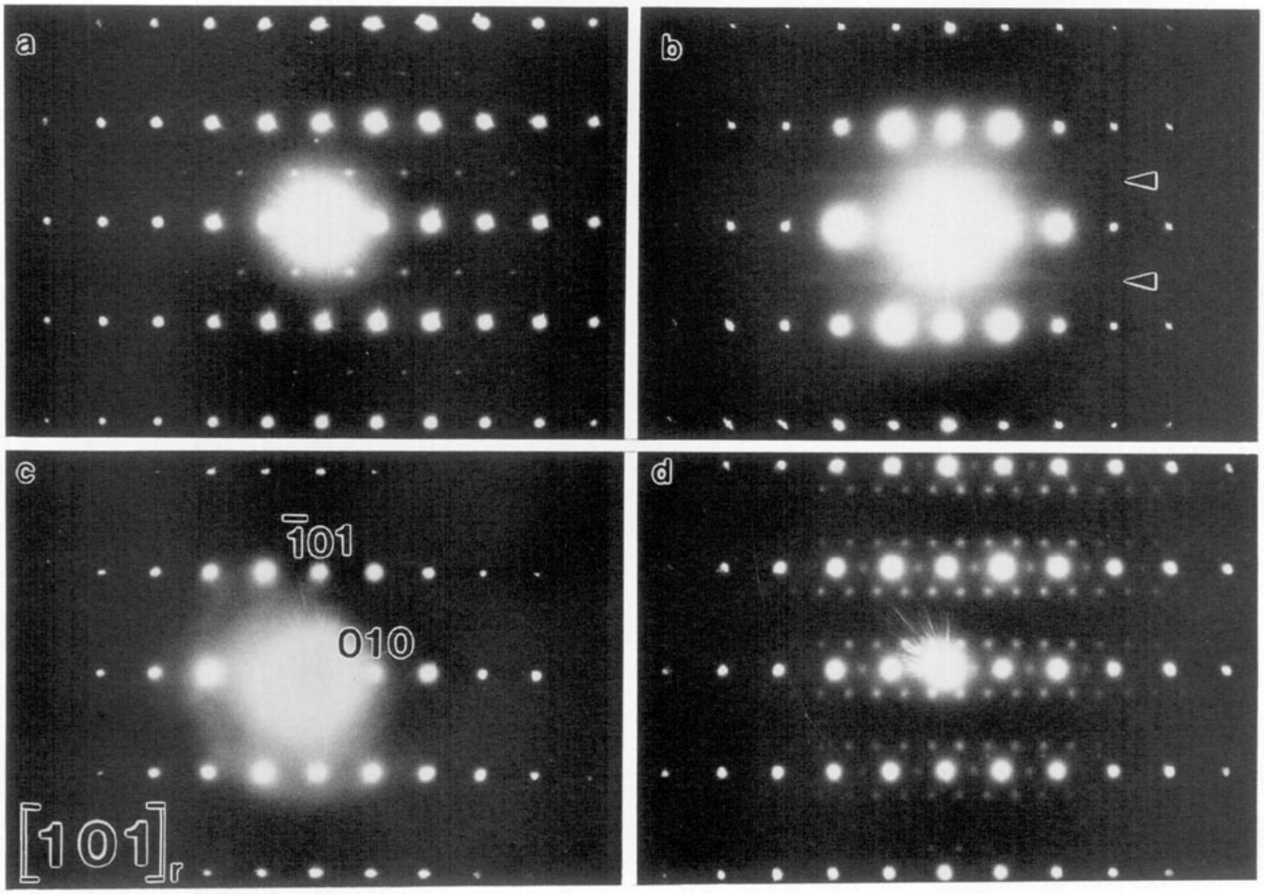

FIG. 2. Selected area electron diffraction patterns along $[101]_{\text{rutile}}$ for ≈SbVO$_4$ prepared from equimolar V$_2$O$_5$/Sb$_2$O$_3$ mixtures at different oxygen partial pressures: (a) $<10^{-11}$ atm, (b) 0.01 atm, (c) 0.03 atm, (d) 1.00 atm.

served. In the reduced samples prepared at $P(O_2) < 0.01$ atm, after careful study of the reciprocal lattice by electron diffraction, the rutile supercell $\sqrt{2}a$, $\sqrt{2}b$ and $2c$ was observed; see Fig. 2a. This superstructure was too weak to be detected in the powder X ray diffraction pattern. For crystals prepared at $P(O_2) = 0.01$ atm, the superstructure spots smear out, giving rise to the diffuse intensity marked by arrows in Fig. 2b. For $\approx SbVO_4$ prepared at intermediate oxygen pressures, $0.01 < P(O_2) < 0.21$ atm, electron diffraction does not show any deviation from a normal rutile-type of lattice; cf Fig. 2c for $\approx SbVO_4$ prepared at 0.03 atm.

A different kind of satellite diffraction spot appears in $\approx SbVO_4$ crystals prepared under a partial oxygen pressure equal to or higher than that for air, i.e., $0.21 < P(O_2) < 1.00$ atm; see Fig. 2d. They can be interpreted as being produced by an almost commensurate, 3 dimensional, structural modulation and the corresponding reciprocal lattice is characterized by reflections of the form $\mathbf{G} \pm m\mathbf{q}$, where $\mathbf{G}$ corresponds to the basic rutile reflections, m is an integer, and $\mathbf{q}$ are the primary modulation wave vectors, given by

$$\mathbf{q} \approx \pm(1/4)\mathbf{a}^* \pm (1/4)\mathbf{b}^* \pm (1/4)\mathbf{c}^*.$$

Careful measurement of the diffraction patterns shows that the modulation is slightly incommensurate along $\mathbf{c}^*$ but commensurate along $\mathbf{a}^*$ and $\mathbf{b}^*$. Therefore, it can also be described as a modulation along $\mathbf{c}^*$ of the rutile supercell $2\sqrt{2}a$, $2\sqrt{2}b$, c. Nevertheless, further work has shown that under slightly different conditions, it was possible to prepare similar crystals exhibiting satellite spots, which were clearly incommensurate along all three reciprocal directions.

Reduced series. Electron microscopy studies of the reduced rutile series with varying nominal V : Sb content show for the vanadium-poor members (nominal V : Sb = 1 : 1 and 1.25 : 1 in Fig. 1) the same $\sqrt{2}a$, $\sqrt{2}b$ and $2c$ superstructure as described previously. The intermediate member with nominal V : Sb = 2 : 1 exhibited an ordinary rutile-type electron diffraction pattern. For the vanadium-rich sample, with a nominal V : Sb atomic ratio equal to 10, powder X ray diffraction revealed that the sample was biphasic. It was mostly composed of a rutile-type phase, with minor amounts of a pure vanadium oxide, according to the EDX analysis. Electron diffraction of the rutile phase in this sample shows main diffraction spots corresponding to the basic rutile lattice and strong diffuse intensity between Bragg spots; see Fig. 3.

3.3. *Crystal Chemical Analyses*

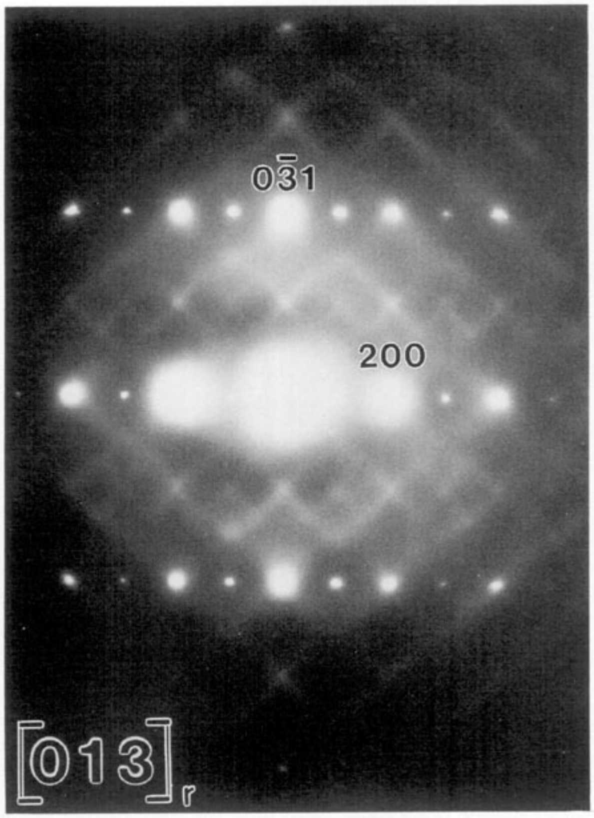

FIG. 3. Selected area electron diffraction pattern along $[013]_{\text{rutile}}$ for $\approx SbVO_4$ prepared from a 10 : 1 V_2O_5/Sb_2O_3 mixture at an oxygen partial pressure of $<10^{-11}$ atm. Unit cell: $a = 4.5617(5)$, $c = 2.9942(5)$ Å, and EDX composition $Sb_{0.2}V_{1.8}O_4$.

General considerations. For the elemental analysis of the rutile material in the first continuous series prepared with nominal V : Sb = 1 (Table 1), a complication is the formation of biphasic samples. The obvious solution to this problem is to prepare phase-pure samples of the end members in the series, and some single-phase near-end-member preparations are presented in Table 2. Phase-pure, oxidized members are easily prepared in air, or pure O_2, and the unit cell content is determined (10) when the V/Sb ratio (nominal or EDX), O/(V + Sb) ratio (TGA), and structure are known. However, a knowledge of the structure can be substituted by a density measurement; see Table 2. On the other hand, preparation under reduc-

TABLE 2

Densities (*d*) of Pure $\approx SbVO_4$ Phases Calculated from Composition and Unit Cell Size and Compared to Densities Observed Using a Gas Pycnometer

Atmosphere	Composition	d_{calc}/g cm^{-3}	d_{obs}/g cm^{-3}
Oxygen	$Sb_{0.92}V_{0.85}O_4$	5.60	5.38
Air	$Sb_{0.92}V_{0.92}O_4$	5.69	5.43
Pure nitrogen	$Sb_{0.78}V_{1.22}O_4$[a]	5.74	5.76

[a] As determined by X ray microanalysis, nominally $Sb_{0.89}V_{1.11}O_4$, i.e., V : Sb = 1.25.

ing conditions is complicated by the fact that substantial amounts of Sb-oxide sublimate and are deposited in colder parts of the flowing-gas system, as previously reported in Ref. (9). Consequently, the single-phase rutile formed will be richer in vanadium than is indicated by the nominal starting composition; cf. the reduced phase prepared in oxygen-free nitrogen in Table 2. Unfortunately, this also means that the oxygen/metal ratio cannot be determined by TGA.

EDX analysis of equimolar series. Due to the complications outlined, the atomic V/Sb ratio of the rutile phase in the samples was quantified using X ray microanalysis (thin film method). The advantage of this method is that the electron probe can be made small enough, such that only $\approx SbVO_4$ and not α-Sb_2O_4 is analyzed. The identity of the $\approx SbVO_4$ was always first confirmed by diffraction and the crystal was then tilted off axis in order to avoid the influence of possible channeling effects on the analyses. A disadvantage with EDX analyses is that the standard deviation in analyzed V/Sb ratio is relatively large, compared to the small V/Sb variation expected in this $\approx SbVO_4$ series.

The EDX results obtained on rutile-type crystals in the 1 : 1 series of samples are presented in Fig. 4, where the oxidized rutiles exhibit a reasonable method-related spread in V/Sb ratios, while the reduced rutiles are clearly not homogeneous. The reduced $\approx SbVO_4$ samples, prepared at oxygen pressures of 5×10^{-6} and $<10^{-11}$ atm, show clear evidence of two compositional populations, i.e., V : Sb = 1.2–1.3 and V : Sb = 1.4–1.5. The sample prepared in an atmosphere with $P(O_2) < 10^{-11}$ atm also shows evidence of the formation of crystals even richer in vanadium. For reasons to be discussed later, it is reasonable to assume the vanadium-poor of the two compositions as belonging to the first series of rutiles. In Fig. 5 the average V/Sb ratios and the unit cell data have been combined. In the two reduced samples with split populations, values with V : Sb < 1.35 have been averaged. A continuous variation in cell parameters as a function of cation composition is revealed for the $\approx SbVO_4$ materials in the 1 : 1 series of samples.

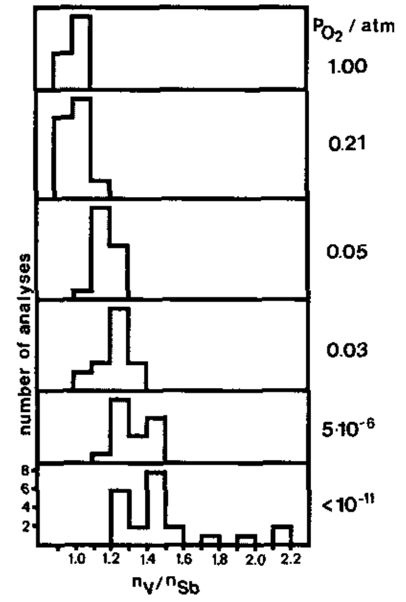

FIG. 4. Histogram of X ray microanalysis results of $\approx SbVO_4$ prepared from equimolar V_2O_5/Sb_2O_3 mixtures at different oxygen partial pressures.

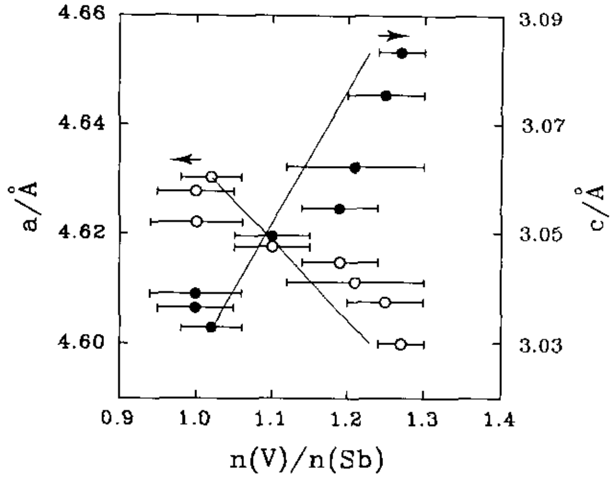

FIG. 5. Cell parameters a (empty circles) and c (filled circles) versus average molar ratio V : Sb in $\approx SbVO_4$ prepared from equimolar V_2O_5/Sb_2O_3 mixtures. Horizontal bars mark ±1 standard deviation in V : Sb ratio determined by EDX. Lines correspond to a hypothetical Vegard-law-type behavior in $Sb_{0.9}V_{0.9+x}O_4$, $0 < x < 0.2$.

3.4. *Infrared Spectroscopy*

Infrared spectra of $\approx SbVO_4$ prepared under different partial pressures of oxygen are shown in Fig. 6. In the spectral region below 800 cm^{-1}, the sample prepared in air (spectrum b) gives bands which are typical of rutiles (11, 12) at 362, 554, and 671 cm^{-1}, with a shoulder at 726 cm^{-1}. Bands at almost identical positions are observed for the samples prepared at low oxygen pressures (spectra c and d). The sample prepared in pure oxygen (spectrum a) and that prepared in pure nitrogen (spectrum e) also show similar features, but the bands are now perturbed by additional weak bands, which possibly are due to the ordering phenomena observed in these two samples. Two additional bands at 880 and 1016 cm^{-1}, with a shoulder at 1000 cm^{-1}, are apparent in the spectra of samples prepared in the presence of oxygen. These bands are not typical of stoichiometric rutiles, where the oxygens in the structure are exclusively coordinated to three metal atoms (11, 12). The fact that the bands decrease in intensity with decreasing oxygen content in the synthesis atmosphere,

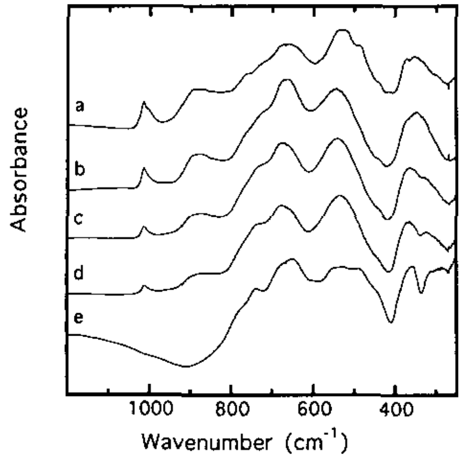

FIG. 6. IR transmission spectra of ≈$SbVO_4$ prepared at 800°C under an atmosphere with the partial pressure of oxygen equal to (a) 1.00 atm, (b) 0.21 atm, (c) 0.05 atm, (d) 0.03 atm, and (e) $<10^{-11}$ atm. The samples in (b) to (e) were prepared by heating an equimolar V_2O_5/Sb_2O_3 mixture, while the single-phase sample in (a) was prepared from a mixture with V/Sb = 0.85/0.92.

and that they are completely absent in the sample prepared in pure nitrogen gas, suggests that these bands are associated with vibrational modes involving the two-coordinated oxygen atoms that are present in the structure due to cation vacancies (10). Crystalline V_2O_5 has two infrared bands at 820 and 1020 cm^{-1}, which are from the metal–oxygen stretching modes involving the one-coordinated and the two-coordinated lattice oxygens, respectively (13). The bands for ≈$SbVO_4$ at 880 and 1016 cm^{-1} are clearly not from V_2O_5 contamination, a conclusion confirmed by the absence of V_2O_5 bands in the corresponding Raman spectra. Moreover, the characterization of the samples with electron microscopy, EDX analysis, and X ray diffraction did not give evidence for any trace of V_2O_5. It is presently not possible to present a definite assignment for the high-frequency bands of ≈$SbVO_4$.

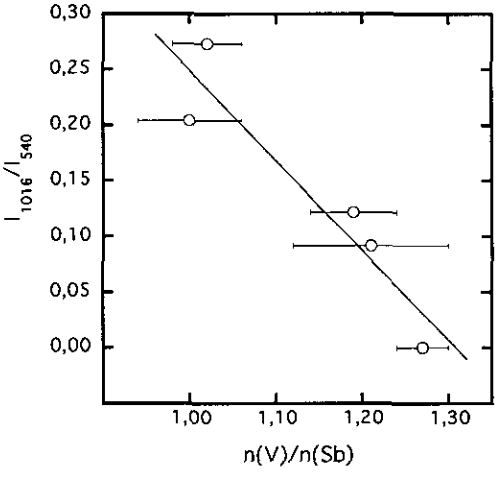

FIG. 7. Intensity of the IR band at 1016 cm^{-1} relative to that at ≈540 cm^{-1} plotted versus the V/Sb ratio determined by EDX.

Figure 7 shows the variation, with the V/Sb ratio, of the intensity of the infrared band at 1016 cm^{-1} relative to the band at 540 cm^{-1}. As mentioned before, the infrared band at 1016 cm^{-1} is not typical, while the band at 540 cm^{-1} is typical, for stoichiometric rutile-type solids. The plot shows a linear dependence within one standard deviation in the V/Sb ratio as determined by EDX analysis. Such a dependence is supportive of the notion that ≈$SbVO_4$ in the 1 : 1 preparations belong to the same series and also indicates that the phase prepared in pure nitrogen is free of vacancies.

4. DISCUSSION

4.1. Solid Solutions

Equimolar series. In deriving a formula for the first ≈$SbVO_4$ series found in the 1 : 1 samples, it is relevant first to consider the pure phase prepared in air, which in a structural study (10) was determined to be $Sb_{0.92}V_{0.92}O_4$. The density 5.43 g cm^{-3} observed by pycnometry is slightly lower than 5.69 g cm^{-3}, which can be calculated for this composition; see Table 2. However, it is noteworthy that the density expected for stoichiometric $SbVO_4$ is 6.04 g cm^{-3} and as high as 6.15 g cm^{-3} for $SbVO_{4.35}$, i.e., a rutile with oxygen in interstitial positions. The density values thus confirm that oxidized ≈$SbVO_4$ has a cation deficiency and not an anion excess or stoichiometric, rutile structure. If instead the pycnometer density 5.43 g cm^{-3} is accepted at face value, the formula $Sb_{0.86}V_{0.86}O_4$ can be calculated.

When an equimolar mixture of Sb_2O_3 and V_2O_5 is heated in pure O_2, see Table 1, the unit cell parameters indicate further oxidation and traces of V_2O_5 are observed, indicating the formation of a rutile phase with slightly less vanadium. Since the previous study (10) suggested that a phase prepared in air can be formulated as $Sb^{5+}_{0.92}V^{4+}_{0.64}V^{3+}_{0.28}\square_{0.16}O_4$, an oxidized phase with only V^{4+} would be $Sb^{5+}_{0.92}V^{4+}_{0.85}\square_{0.23}O_4$. An oxide mixture with V : Sb = 0.85 : 0.92 heated in O_2 produced a pure phase with no trace of V_2O_5 in the powder pattern. The oxygen content determined by TGA corresponded to a composition of $Sb_{0.92}V_{0.85}O_{3.99}$; see Table 2. Although the observed densities of the phases prepared in air and pure O_2, respectively, are slightly low, the composition of the oxidized endmember of the series can safely be formulated as $Sb_{0.9}V_{0.9}O_4$.

Reduction, i.e., a decrease of the average oxidation state of the cations, in this type of material is accomplished by an increase in the number of cations, since the total cation charge is fixed by the constant number of oxide ions in the unit cell. It is clear from the powder diffraction intensities, cf. Table 1, and the EDX analyses, Figs. 4 and 5, that upon reduction the amount of vanadium in the rutile phase increases. Filling all the vacancies in $Sb_{0.9}V_{0.9}\square_{0.2}O_4$ (V : Sb = 1) with vanadium gives the reduced endmember a unit cell content of $Sb_{0.9}V_{1.1}O_4$ and V : Sb = 1.22. The predicted range of V : Sb ratios fits that observed in the X ray microanalyses of rutiles in the 1 : 1 series of samples, when the analytical errors are taken into account; see Fig. 5. This suggests that these rutiles form a continuous nonstoichiometric series $Sb_{0.9}V_{0.9+x}\square_{0.2-x}O_4$, $0 < x < 0.2$. Further support for the existence of a single continuous series of rutiles is offered by the IR data in Fig. 6, where the intensity of the two bands special to $\approx$SbVO$_4$, at 880 and 1016 cm^{-1}, decreases smoothly with increasing reduction. Since it is reasonable to associate the two bands with the metal vacancies in the structure and since their intensities drop to zero at maximum reduction, the reduced endmember should be defect free, as is the case in $Sb_{0.9}V_{1.1}O_4$. According to the formula $Sb_{0.9}V_{0.9+x}\square_{0.2-x}O_4$, the amount of vacancies per unit cell ($\square$) as a function of the atomic ratio V/Sb is

$$\square = -0.9 \cdot (V/Sb) + 1.1.$$

If the IR intensity of a vacancy band relative to a normal rutile band is proportional to the amount of vacancies per unit cell, one would thus expect the IR response to be linearly dependent on the V/Sb ratio and to exhibit a negative slope. This type of behavior is indeed observed in Fig. 7.

Attempts to prepare phase-pure samples of the reduced endmember $Sb_{0.9}V_{1.1}O_4$ in purified N_2 have so far failed; see Table 2. Due to loss of antimony-oxide, a pure phase of composition $Sb_{0.8}V_{1.2}O_4$ (V : Sb = 1.5) is formed instead, according to the EDX analysis and density measurement. The lattice parameters indicate that this phase belongs to the second series of reduced rutiles; see Fig. 1 for nominal V/Sb = 1.25:1. Apparently the presence of α-Sb_2O_4 is needed to prepare endmember $Sb_{0.9}V_{1.1}O_4$, probably by limiting the loss of antimony-oxide to the gas phase. However, the analyses of the sample prepared at $P(O_2) < 10^{-11}$ atm in Fig. 4 in fact suggest that even if α-Sb_2O_4 is present, $Sb_{0.9}V_{1.1}O_4$ with time decomposes to form a more vanadium-rich phase with V : Sb = 1.4–1.5. The crystalline areas of the vanadium-rich decomposition product formed in this case must be quite small, since no X ray lines corresponding to this phase were observed. On the other hand, if the decomposition product occurs as small crystals or as a surface phase it might well be overrepresented in the EDX analysis, since thin crystal edges are exclusively selected when performing X ray microanalysis in a transmission electron microscope.

Reduced series. The results indicate that the second series of rutiles consists of a solid solution series toward VO_2, forming at low partial pressures of O_2. It can be formulated as $Sb_{0.9-y}V_{1.1+y}O_4$, $0 < y < 0.7$, since it extends to $Sb_{0.2}V_{1.8}O_4$ at 800°C; cf. Fig. 3. Our formulation of the reduced series of rutiles as $Sb_{0.9-y}V_{1.1+y}O_4$, i.e., a solid solution without vacancies, is also supported by two observations made by Berry *et al.* (9), though their interpretation was different. First, reaction in flowing commercial N_2, producing up to kilogram amounts of reduced $\approx$SbVO$_4$ (a = 4.60, c = 3.08 Å) and α-Sb_2O_4 (orthorhombic), could be accomplished without weight change. Second, reaction in a closed tube of a 1 : 1 mixture of Sb_2O_3 and V_2O_5 produced the reduced type of $\approx$SbVO$_4$ (cell apparently similar to that above) and minor amounts of β-Sb_2O_4 (monoclinic). A reaction not involving gaseous oxygen can actually be written using any member of the solid solution $Sb_{0.9}V_{1.1}O_4$–$Sb_{0.2}V_{1.8}O_4$. Since the cell parameters reported are consistent with those we observe for the vanadium-poor endmember, the reaction can be written as

$$Sb_2O_3 + V_2O_5 \rightarrow 1.82\,Sb_{0.9}V_{1.1}O_4 + 0.18\,Sb_2O_4.$$

The existence of a solid solution $Sb_{0.9}V_{1.1}O_4$-$Sb_{0.2}V_{1.8}O_4$ can explain the observation made by Nilsson *et al.* (7, 14) that a fresh catalyst containing $\approx$SbVO$_4$ and V_2O_5, after use in the reactor, only exhibited $\approx$SbVO$_4$ powder diffraction peaks. If the reaction conditions are sufficiently reducing, the vanadium oxide can simply dissolve in the rutile phase.

4.2. *Oxidation States*

The question of oxidation states of the metal ions in nonstoichiometric SbVO$_4$ has been subject to some controversy and is of great importance for the interpretation of catalytic mechanisms. The substitution mechanism in the first series of $\approx$SbVO$_4$ rutiles prepared from equimolar mixtures

$$3\,V^{4+} + \square \leftrightarrow 4\,V^{3+}$$

implies controlling the amount of V^{4+} reduced to V^{3+}, as well as the amount of vacancies, by changing of the partial oxygen pressure $P(O_2)$. The second series of $\approx$SbVO$_4$, prepared from oxide mixtures of increasing vanadium content in pure N_2 flow, follows the substitution

$$Sb^{5+} + V^{3+} \leftrightarrow 2\,V^{4+},$$

i.e., the overall cation valence is maintained (no vacancies are generated), but the Sb/V ratio changes. A third curve connecting the two investigated $\approx$SbVO$_4$ series would utilize the substitution mechanism

$$5\ V^{4+} \leftrightarrow 4\ Sb^{5+} + \square.$$

It is indeed possible to prepare $\approx$SbVO$_4$ samples falling in the area between the curves, at least close to where the two series meet in Fig. 1.

Bringing the oxidation states into the formulas gives, for the first (1 : 1) series,

$$Sb^{5+}_{0.9}V^{4+}_{0.8-3x}V^{3+}_{0.1+4x}\square_{0.2-x}O_4,\ 0 < x < 0.2$$

and for the second (reduced) series,

$$Sb^{5+}_{0.9-y}V^{4+}_{0.2+2y}V^{3+}_{0.9-y}O_4,\ 0 < y < 0.7.$$

Thus, the oxidized endmember of the first (1 : 1) series becomes $Sb^{5+}_{0.9}V^{4+}_{0.8}V^{3+}_{0.1}\square_{0.2}O_4$ ($x = 0$), with predominantly V(IV), while the reduced endmember is $Sb^{5+}_{0.9}V^{4+}_{0.2}V^{3+}_{0.9}\square_{0.0}O_4$ ($x = 0.2$), with almost all V(III). The V-rich end of the second (reduced) series becomes $Sb^{5+}_{0.2}V^{4+}_{1.6}V^{3+}_{0.2}O_4$, which is approaching $V^{4+}O_2$.

The formulas above include oxidation states Sb(V), V(III), and V(IV), but not Sb(III) or V(V), in general agreement with previous studies of $\approx$SbVO$_4$ prepared from equimolar V/Sb oxide mixtures. Magnetic susceptibility measurements, probably on a reduced phase, excluded the combination of Sb(III) and V(V) (15). Mössbauer spectroscopy of the oxidized and the reduced phases showed the presence of Sb(V) and the absence of Sb(III) in both materials (8). Bond valence summations disclosed that the oxygen octahedron in the oxidized phase is not suitable for Sb(III) and V(V), while Sb(V), V(III), and V(IV) are readily accommodated (10). An electron spin resonance study revealed the presence of a V(IV) signal from the oxidized material, but not for the reduced material (16). The absence of a vanadium(IV) signal in the latter case can possibly be due to coupling phenomena.

4.3. *Ordering*

In a recent review, Baur (17), lists not less than 16 structure types derived from the basic rutile structure, of which 7 are based on cation ordering, 3 on anion ordering, and 6 on distortions of the structure. The supercell ($\sqrt{2}a$, $\sqrt{2}b$, $2c$) observed here for reduced $\approx$SbVO$_4$ is known for MgUO$_4$, but a convergent beam electron diffraction study of the reduced $\approx$SbVO$_4$ (Landa-Cánovas *et al.* to be published) has shown that the symmetry is higher than that of MgUO$_4$, which is orthorhombic *Imam* (17). The modulated structure of oxidized $\approx$SbVO$_4$ corresponds approximately to a rutile supercell $2\sqrt{2}a$, $2\sqrt{2}b$, $4c$, which has not been observed before (17). The structural basis of the two new rutile supercells of $\approx$SbVO$_4$ is presently being investigated by electron microscopy and Rietveld refinements of X ray powder data (Landa-Cánovas *et al.*, to be published).

The fact that it is almost impossible to observe any rutile superlattice reflections in the X ray powder diffraction patterns suggests the presence of only soft ordering of cations and vacancies in the endmember phases. Nevertheless, by electron diffraction we observe an order–disorder–order transition as a function of oxidation level in the first (1 : 1) series. Close inspection of the lattice parameters in Fig. 1 reveals two slight changes of slope at 0.01 and 0.21 atm, respectively, in the c vs a curve for the 1 : 1 series. Changes of slope could be related to the order–disorder transitions observed by electron diffraction close to these two partial pressures of oxygen. In the second (reduced) series, a transition from order to disorder occurs as a function of increasing vanadium content, though the diffuse intensity in the diffraction patterns of the vanadium-rich, disordered endmember (Fig. 3) suggests the presence of atomic correlations in the structure.

5. CONCLUSIONS

In conclusion, heating of equimolar mixtures of Sb$_2$O$_3$ and V$_2$O$_5$ at 800°C in flowing gas with varying O$_2$/N$_2$ partial pressures produces a nonstoichiometric series $Sb_{0.9}V_{0.9+x}\square_{0.2-x}O_4$, $0 < x < 0.2$, and minor amounts of α-Sb$_2$O$_4$. In contrast to our single series, the same situation is interpreted as not less than three series in Ref. (9), i.e., one oxidized series and two reduced series, all with SbVO$_4$ as an endmember. No experimental results corresponding to the series that we interpret as a reduced solid solution $Sb_{0.9-y}V_{1.1+y}O_4$ have been reported before, since the previous studies (8, 9) were performed using equimolar mixtures of Sb$_2$O$_3$ and V$_2$O$_5$.

Although some of the crystal chemical limits of $\approx$SbVO$_4$ reported here are not so precisely determined as one could have wished, the general redox behavior of bulk $\approx$SbVO$_4$ is now definitely better understood. In order to precisely map out the compositional field of this phase at different temperatures, equilibrium experiments are needed. These experiments will have to take into account, not only the oxygen pressure, but also the partial pressures of gaseous Sb–oxide species.

ACKNOWLEDGMENTS

We thank the Swedish Natural Science Research Council (NFR) and the Swedish Research Council for Engineering Sciences (TFR) for financial support. We also thank Professor B. G. Hyde and Dr. L. C. Otero-Diaz for stimulating discussions concerning cation deficient rutiles.

REFERENCES

1. B. G. Hyde and S. Andersson, "Inorganic Crystal Structures." Wiley, New York, 1989.
2. G. Centi, F. Trifirò, and R. K. Graselli, *Chem. Ind. (Milan)* **72,** 617 (1990).
3. J. F. Roth, *in* "Catalytic Science and Technology" (S. Yoshida, N. Takezawa, and T. Ono, Eds.), Vol. 1, p. 3. Kodansha, Tokyo, 1991.
4. U. S. Patents 4,746,641 (1988); 4,784,979 (1988); 4,788,317 (1988); 4,801,568 (1989); 4,871,706 (1989); 4,879,264 (1989).
5. A. Andersson, S. L. T. Andersson, G. Centi, R. K. Graselli, M. Sanati, and F. Trifirò, *in* "New Frontiers in Catalysis, Proceedings, 10th International Congress of Catalysis" (L. Guszi, F. Solymosi, and P. Tétényi, Eds.), Studies in Surface Science and Catalysis, Vol. 75, p. 691. Elsevier, Amsterdam, 1993.
6. G. Centi, R. K. Graselli, E. Patane, and F. Trifirò, *in* "New Developments in Selective Oxidation" (G. Centi and F. Trifirò, Eds.), Studies in Surface Science and Catalysis, Vol. 55, p. 515. Elsevier, Amsterdam, 1990.
7. R. Nilsson, T. Lindblad, and A. Andersson, *J. Catal.* **148,** 501 (1994).
8. T. Birchall and A. W. Sleight, *Inorg. Chem.* **15,** 868 (1976).
9. F. J. Berry, M. E. Brett, and W. R. Patterson, *J. Chem. Soc. Dalton Trans.* 9 (1983).
10. S. Hansen, K. Ståhl, R. Nilsson, and A. Andersson, *J. Solid State Chem.* **102,** 340 (1993).
11. C. Rocchiccioli-Deltcheff, T. Dupuis, R. Franck, M. Harmelin, and C. Wadier, *C.R. Acad. Sci. Paris Ser. B* **270,** 541 (1970).
12. E. Husson, Y. Repelin, H. Brusset, and A. Cerez, *Spectrochim. Acta Part A* **35,** 1177 (1979).
13. L. Abello, E. Husson, Y. Repelin, and G. Lucazeau, *Spectrochim. Acta Part A* **39,** 641 (1983).
14. R. Nilsson, T. Lindblad, A. Andersson, C. Song, and S. Hansen, *in* "New Developments in Selective Oxidation II" (V. Cortés Coberán and S. Vic Bellón, Eds), Studies in Surface Science and Catalysis, Vol. 82, p. 293. Elsevier, Amsterdam, 1994.
15. H. Schüer and W. Klemm, *Z. Anorg. Allg. Chem.* **395,** 287 (1973).
16. F. J. Berry and M. E. Brett, *Inorg. Chim. Acta* **76,** L205 (1983).
17. W. H. Baur, *Z. Kristallogr.* **209,** 143 (1994).