Vanadium Antimonate

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The reaction between equimolar quantities of antimony(III) oxide and vanadium(V) oxide at temperatures between 600 and 800 °C is critically dependent on the presence of oxygen. In oxygen-free nitrogen a rutile-type antimony-deficient compound of composition $VSb_{1-y}O_{4-3/2y}$ $(0 < y < 0.1)$ is formed. Antimony(III) oxide which is present in excess of the amount required for formation of this phase is removed by sublimation. Similar reactions in commercial nitrogen or sealed tubes give biphasic products composed of the non-stoicheiometric rutile-type phase containing less oxygen, $VSb_{1-y}O_{4-2y}$ $(0 < y < 0.1)$, and antimony tetroxide. Reactions performed in oxygen give homogeneously oxidised products. The stoicheiometric compound of composition $VSbO_4$ has not been observed in any of the products. The characteristics of the observed reaction products are described and the nature of the solid-state reaction is discussed.

Although the antimony–vanadium–oxygen ternary system has been examined in the past [1-6] considerable confusion persists over such fundamental matters as the nature of the products and the conditions under which they may be formed.

A material with formula '$SbVO_4$' was first reported[1] in 1951 from the equimolar reaction of antimony(III) oxide and vanadium(V) oxide in air at 750 °C. Apparently similar products were obtained from reactions[3] at 600 °C and in sealed tubes at 700[2] or 1 050 °C,[4] whilst biphasic materials were reportedly[2] formed in products quenched from above 800 °C. The most recent investigation[5] has concluded that '$VSbO_4$' contains an antimony oxide phase even when formed under anaerobic conditions. In addition to the confusion connected with the phase composition of these products, the nature of the cationic oxidation states is also a subject of much uncertainty.[3-5]

We have therefore attempted to clarify these matters by examining the products from solid-state reactions between antimony(III) oxide and vanadium(V) oxide under different conditions.

Experimental

Intimately ground mixtures of finely powdered high-purity antimony(III) oxide and vanadium(V) oxide were heated in silica crucibles in flowing nitrogen (BOC oxygen-free grade) which had been dried at 77 K and by passing over phosphorus pentoxide. In some experiments the nitrogen was passed over manganese(II) oxide supported on Celite[7] to reduce the concentration of residual oxygen to, at most, 1 part in $10^{9.5}$. The reaction mixture was heated to 600 °C over 12 h, maintained at this temperature for a further 12 h, increased to 750 °C over 6 h, and finally maintained at this temperature for an additional 24 h. Similar experiments were performed in air and in sealed tubes.

X-Ray diffraction photographs were obtained with a Guinier de Wolff camera (diameter 228 mm) and diffraction data were recorded with a Philips vertical goniometer (PW 1050/70) using Cu-K_α radiation. Scanning-electron micrographs were obtained with Cambridge Stereoscan S4 and JEOL JSM-35 instruments. E.s.r. spectra were recorded at 298 K with a Hilger and Watts instrument operating at 9.4 GHz. Thermogravimetric and differential thermal investigations were performed with a Linseis GmbH apparatus with a heating rate of 10 °C min^{-1}.

Table 1. *X*-Ray diffraction data for monophasic vanadium antimonate

Intensity	*hkl*	*d*/Å Obs.	*d*/Å Calc.
100	110	3.238	3.253
57	101	2.546	2.558
15	200	2.287	2.300
9	111	2.227	2.236
2	210	2.049	2.057
45	211	1.708	1.710
13	220	1.623	1.626
6	002	1.538	1.539
9	310	1.453	1.455
9	112	1.391	1.391
13	301	1.371	1.372
4	202	1.278	1.279

Unit-cell dimensions: $a = b = 4.600 \pm 0.004$, $c = 3.078 \pm 0.004$ Å.

Results

Reactions in Oxygen-free Nitrogen.—The reaction between equimolar quantities of white antimony(III) oxide and orange vanadium(V) oxide in flowing nitrogen, freed of any residual oxygen by passage over manganese(II) oxide,[7] gave a black crystalline product. The reaction was accompanied by the sublimation of a white crystalline material which *X*-ray diffraction showed to be cubic antimony(III) oxide. The occurrence of sublimation was independent of the rate of heating. The *X*-ray diffraction pattern recorded from the black product prepared at 750 °C showed an absence of peaks previously observed in the diffraction patterns of materials derived from other preparations and attributed to polymorphs[2] of '$VSbO_4$' or to the 001 plane in the material described[5] as $V_{1.05}Sb_{0.95}O_4$. The *X*-ray diffraction pattern from our product gave no evidence for the presence of unreacted antimony(III) oxide or vanadium(V) oxide. No trace of antimony tetroxide, which was detected in small amounts in materials formed at 600 °C, was recorded. The *X*-ray diffraction data for the product formed at 750 °C were indexed according to a tetragonal unit cell (Table 1) and may be described as those of a rutile-type solid with unit-cell parameters $a = b = 4.600 \pm 0.004$ and $c = 3.078 \pm 0.004$ Å, which may be compared with those previously attributed (Table 2) to stoicheiometric [1-4]

Table 2. Unit-cell dimensions (Å) reported for 'vanadium antimonate'

a	b	c	Ref.
4.58	4.58	3.06	1
4.598	4.598	3.078	2
4.631	4.631	3.046	3
4.605	3.065	3.595 *	4
6.5289	6.5061	4.0839 †	5
4.6241	4.6241	3.0369 ‡	5

* $\gamma = 90.25°$; subsequently corrected[5] to $a = 4.605$, $b = 4.595$, and $c = 3.065$ Å. † Described as $V_{1.05}Sb_{0.95}O_4$. ‡ Described as $V_{0.92}Sb_{0.92}O_4$.

Table 3. *X*-Ray diffraction data for $VSb_{1-y}O_{4-2y}$ + α-Sb_2O_4 formed at 750 °C

		Orthorhombic		Tetragonal	
Intensity	$d_{obs.}$/Å	*hkl*	$d_{calc.}$/Å	*hkl*	$d_{calc.}$/Å
8	3.440 [a]				
100	3.249	200	3.255	110	3.256
19	3.079	001	3.083	[b]	[b]
7	2.950 [a]				
8	2.936 [a]				
4	2.722 [a]				
10	2.656 [a]				
71	2.564	111	2.562	101	2.563
6	2.468 [a]				
6	2.401 [a]				
19	2.304	220	2.302	200	2.303
12	2.235	201	2.238	111	2.239
6	2.058	130 310	2.059 2.059	210	2.059
7	1.863 [a]				
7	1.781 [a]				
64	1.713	311 131	1.712 1.712	211	1.713
33	1.627	400 040	1.627 1.628	220	1.628
3	1.591 [a]				
8	1.542	002	1.542	002	1.543

[a] α-Sb_2O_4.[15] [b] See text for discussion. Orthorhombic cell dimensions: $a = 6.509 \pm 0.01$, $b = 6.512 \pm 0.01$, $c = 3.083 \pm 0.005$ Å. Tetragonal cell dimensions $a = b = 4.605 \pm 0.008$, $c = 3.085 \pm 0.005$ Å.

and non-stoicheiometric[5] vanadium antimonate. The present results support the assertion[5] that the reported formation of stoicheiometric vanadium antimonate[2] at 750 °C is erroneous. We would also suggest that the product is not formed at 600 °C as has been reported.[3] However, in contrast to the most recent report,[5] we believe that the black product is monophasic and may be represented by the formulation $VSb_{1-y}O_{4-3/2y}$ where $0 < y < 0.1$ and is illustrative of the antimony(III) oxide lost by sublimation.

Reactions in Commercial Nitrogen.—Equimolar reactions between antimony(III) oxide and vanadium(V) oxide under similar conditions but in commercial nitrogen from which residual oxygen was not removed gave biphasic products which were shown by *X*-ray diffraction to contain a rutile-type phase and α-Sb_2O_4. Above 800 °C the antimony tetroxide was formed in the β form. The course of the reaction was essentially similar to that described earlier and the preparative procedure was successful for quite large quantities (*ca.* 4 mol) of material with weight changes as low as 3×10^{-5}% normally recorded. The detection of antimony tetroxide in the *X*-ray diffraction pattern suggests that some oxidation of antimony(III) to antimony(V) occurs during the reaction despite the presence of nitrogen and implies antimony deficiency in the rutile-type phase. The *X*-ray diffraction pattern gave no evidence for the presence of unreacted vanadium(V) oxide or other oxides of vanadium and e.s.r. measurements failed to detect the presence of paramagnetic vanadium(IV).

A typical set of *X*-ray diffraction data for the biphasic products formed at 750 °C is given in Table 3. The unit-cell parameters, calculated according to a tetragonal unit cell, $a = b = 4.605 \pm 0.008$ and $c = 3.085 \pm 0.005$ Å, are, within experimental limits, in agreement with those obtained for the monophasic rutile-type product. Whilst the two vanadium antimonate phases are probably of similar structure, measurements of the extent of antimony tetroxide formation in the biphasic product were indicative of a reduced form of the monophasic material with a composition more accurately described as $VSb_{1-y}O_{4-2y}$ where $0 < y < 0.1$.

Thermogravimetric analysis of the biphasic product in argon showed that an initially slow loss of weight increased at *ca.* 800 °C and continued until the solid melted at 905 °C. Presumably the loss in weight at higher temperatures reflects the volatilisation of Sb_2O_4 as has been observed during the thermal treatment of other biphasic systems containing rutile-type and Sb_2O_4 phases.[8] We found no evidence to support the reported[3] decomposition of the rutile-type phase into V_2O_5 and Sb_2O_3 on melting in an inert atmosphere. Furthermore, thermogravimetric analysis and differential thermal analysis in air did not confirm the reported[3] uptake by '$SbVO_4$' of oxygen between 450 and 500 °C and the formation of a material of composition $Sb_2V_2O_9$. The reported[3] fixation of free oxygen may be more reasonably associated with the oxidation of unreacted Sb_2O_3 and is quite consistent with our *X*-ray and electron-microscope evidence for the presence of large quantities of Sb_2O_4 in products formed from incomplete reactions below 600 °C.

All reactions between non-equimolar quantities of antimony(III) oxide and vanadium(V) oxide in commercial nitrogen produced rutile-type phases which gave *X*-ray diffraction patterns similar to the antimony-deficient vanadium antimonate. However, materials formed in vanadium-rich systems also contained unreacted vanadium(V) oxide, whilst those obtained from antimony-rich systems contained α-Sb_2O_4.

Reactions in Sealed Tubes.—Reactions between equimolar quantities of antimony(III) oxide and vanadium(V) oxide in sealed, but not evacuated, tubes gave biphasic products containing Sb_2O_4 and the reduced antimony-deficient rutile-type material. It seems reasonable therefore that other materials which have previously[2,5] been described as '$VSbO_4$', following reactions in evacuated sealed tubes between 700 and 800 °C, were similar to our biphasic products. Furthermore we contend that the *X*-ray lines which have been attributed[2] to a high-temperature polymorph of '$VSbO_4$' formed in a sealed tube between 800 and 865 °C correspond more closely to those[9] of β-Sb_2O_4 and that the material prepared[4] at 1 050 °C in a sealed tube was of similar biphasic composition.

Reactions in Air.—Reactions between equimolar ratios of antimony(III) oxide and vanadium(V) oxide in air were accompanied by at least partial oxidation of antimony(III) oxide to Sb_2O_4. The reaction between Sb_2O_4 and vanadium(V) oxide was very slow and at 700 °C gave only a semi-fused mixture of components. At higher temperatures oxidation gave a small increase in weight and a product which scanning-electron microscopy and *X*-ray diffraction showed to be a homogeneous material and which we presume corresponds to that previously[5] formulated as $V_{1-y}Sb_{1-y}O_4$ ($0 < y < 0.1$). Similar products were also obtained by heating either monophasic vanadium antimonate or the biphasic material containing the antimony-deficient rutile phase in air at 750 °C for 24 h. The *X*-ray diffraction pattern of a sample of composition $V_{0.91}Sb_{0.91}O_4$ gave cell parameters, calculated according to a tetragonal unit cell, of $a = b = 4.624 \pm 0.016$ and $c = 3.043 \pm 0.014$ Å which are in good agreement with those calculated[1] for '$SbVO_4$' and the material more recently described[5] as $V_{0.92}Sb_{0.92}O_4$.

Discussion

The reaction between antimony(III) oxide and vanadium(V) oxide to give stoicheiometric vanadium antimonate appears to be less facile than might be expected. It would seem that a number of rutile-type non-stoicheiometric modifications of vanadium antimonate are formed with compositions depending on the experimental conditions. We contend that the reaction between antimony(III) oxide and vanadium(V) oxide in air does not lead to the formation of a monophasic product of composition '$SbVO_4$' as has been claimed by earlier workers.[1] It would seem that the single-phase product formed in an appreciable supply of oxygen results from homogeneous oxidation of the bulk and the formation of a compound which may be described[5] by the formulation $V_{1-y}Sb_{1-y}O_4$.

However, in contrast to the most recent report,[5] we propose that monophasic vanadium antimonate may be prepared by slowly heating the reactants in a strictly oxygen-free environment. It is interesting that the reaction proceeds without the formation of a melt even though the reaction temperature exceeds the melting point of the individual reactants. The cause of non-stoicheiometry in vanadium antimonate presumably occurs in the course of the reaction and may result from the solubility of Sb_2O_3 in V_2O_5 being less than 1 : 1. Under such circumstances the unreacted Sb_2O_3 would remain in the reaction mixture in oxygen-free nitrogen and its subsequent volatilisation result in the formation of the antimony-deficient rutile-type product formulated as $VSb_{1-y}O_{4-3/2y}$.

The formation of biphasic materials containing antimony tetroxide when oxygen [<10 p.p.m. (v/v)] is present in the nitrogen gas flow reflects the sensitivity of the system to molecular oxygen. However, the quantity of antimony tetroxide formed during such reactions requires more oxygen than may reasonably be expected to be present in commercial nitrogen. More importantly, the uptake by antimony(III) oxide of oxygen by this means would readily be revealed by overall increases, of the order of *ca.* 1.5%, in the weight of the products. In this respect it is relevant to note that although vanadium(V) oxide loses[10] oxygen above the melting point of 690 °C, the material, when heated in the presence of other oxides, has been reported[11-13] to evolve oxygen at temperatures as low[11] as 565 °C. We therefore suggest that, in addition to the direct oxidation of antimony(III) oxide by molecular oxygen, a significant proportion of the antimony tetroxide formed in products from reactions in impure nitrogen and showing minimum weight changes results from an alternative mechanism involving the reduction of vanadium(V) oxide. In this respect it is pertinent to record that evidence for the presence of V_2O_3 was found in the *X*-ray diffraction pattern recorded from a product containing large quantities of Sb_2O_4.

The absence of Sb_2O_4 in the monophasic vanadium antimonate formed from reaction of Sb_2O_3 and V_2O_5 in strictly oxygen-free nitrogen suggests that Sb_2O_3 itself is unable to induce labilisation of oxygen from V_2O_5. It is therefore interesting to note that the low-temperature reduction of V_2O_5 in the presence of other metal oxides[11,12] has been attributed to the alleviation of crystal strain at coherent solid–solid interfaces and, if similar processes are relevant to the observations reported here, then the crystallographic match of the two components V_2O_5 and Sb_2O_4 may be influential in the reduction phenomenon. Hence the reaction in oxygen-containing nitrogen gives rise to the biphasic product containing a reduced antimony-deficient vanadium antimonate, formulated as $VSb_{1-y}O_{4-2y}$, and $\frac{y}{2}$ Sb_2O_4. The failure of the products to give e.s.r. signals characteristic of paramagnetic vanadium(IV) does not support the suggested[5] formulation of the rutile-type phase as $V^{III}{}_{1-y}V^{IV}{}_{2y}Sb^{V}{}_{1-y}O_4$ and its description as a solid solution between VO_2 and '$VSbO_4$'.

The sensitivity of the reaction to oxygen implies that reactions in sealed tubes[2,4,5] contained sufficient residual oxygen to initiate oxidation of Sb_2O_3 to Sb_2O_4 and give the biphasic product. The failure of Sb_2O_3 and V_2O_5 to give the monophasic product when rapidly heated under anaerobic conditions resembles the formation[14] of $TeVO_4$ from carefully heated mixtures of TeO_2 and VO_2 whilst more severe thermolysis gives $Te_2V_2O_9$ and elemental tellurium. It seems that vigorous heating conditions induce extensive reduction, oxidation, and decomposition processes in such solid-state reactions between oxides.

A number of the results reported here call into question the existence of the material previously described[3] as $Sb_2V_2O_9$. The reactions between V_2O_5 and Sb_2O_3 which give rise to Sb_2O_4 might be expected to be followed by reactions between unreacted V_2O_5 and Sb_2O_4 to give $Sb_2V_2O_9$. Examination of our products by *X*-ray diffraction, scanning-electron microscopy, and i.r. spectroscopy gave no evidence for the presence of such a phase. Furthermore, attempts to repeat the reported[3] preparation of $Sb_2V_2O_9$ yielded the biphasic product of $VSb_{1-y}O_{4-2y}$ and Sb_2O_4. Given the similarity[3] between the *X*-ray diffraction data for vanadium antimonate and those reported for $Sb_2V_2O_9$ the existence of $Sb_2V_2O_9$ must be in some doubt.

X-Ray Investigations of Vanadium Antimonate.—Although all the investigations[1-5] of vanadium antimonate have used powder *X*-ray diffraction methods for the characterisation of the products, the literature shows considerable confusion in the interpretation of the data. The monophasic antimony-deficient rutile-type product $VSb_{1-y}O_{4-3/2y}$ formed during this work from the reaction in oxygen-free nitrogen at 750 °C gave similar cell parameters to those of the reduced rutile-type material of composition $VSb_{1-y}O_{4-2y}$ formed with Sb_2O_4 in impure nitrogen at 750 °C and to those of the oxidised material $V_{1-y}Sb_{1-y}O_4$. The small differences between the lattice parameters of these phases which resemble the unit-cell dimensions attributed to stoicheiometric[1-4] and non-stoicheiometric[5] $VSbO_4$ are presumably a reflection of the slight variations in stoicheiometry between these essentially similar phases.

It is also relevant to note that the treatment of the *X*-ray data itself has been the matter of some discussion. The most recent study[5] reported that a material $V_{1.05}Sb_{0.95}O_4$ quenched from 900 °C without the formation of Sb_2O_4 is not tetragonal and that the *X*-ray diffraction pattern is best indexed according to a *C*-centred orthorhombic cell. Indeed, the calculated spacings of the lattice planes agree with the observed values except that for the 001 plane ($d_{obs.}$ 3.066, $d_{calc.}$ 3.085 Å). We suggest here that the peak attributed[5] to the 001 plane of $V_{1.05}Sb_{0.95}O_4$ would be better ascribed to the 112 plane in α-Sb_2O_4 (3.073 Å)[15] which gives the most intense peak in the α-Sb_2O_4 diffraction pattern. It appears therefore that direct evidence for an Sb_2O_4 impurity phase in the material $V_{1.05}Sb_{0.95}O_4$ has been overlooked. A material prepared at 900 °C during our investigation gave similar *X*-ray diffraction data but a number of the peaks appeared split. In a tetragonal cell $a = b$ and equivalent planes, *e.g.* 130 and 310, give rise to one peak in the *X*-ray diffraction pattern. However, in an orthorhombic cell $a \neq b$ and such planes are no longer equivalent. In the material investigated here and elsewhere[5] $a \approx b$ hence the two planes may be expected to have similar *d* spacings and give rise to a pair of closely spaced peaks which appear as a split single peak in the *X*-ray diffraction pattern. Although the pattern could be indexed to a tetragonal cell the observed splitting of the *X*-ray diffraction peaks suggests that the assignment of a *C*-centred orthorhombic cell to materials formed at these temperatures is superior. We also suggest that the amorphous material detected[5] in these products formed at high temperature is β-Sb_2O_4 which we found to be formed under similar conditions. The *X*-ray diffraction data from our biphasic product formed at 750 °C containing the antimony-deficient rutile-type material $VSb_{1-y}O_{4-2y}$ with an α-Sb_2O_4 phase was amenable to equally valid interpretation by using both the tetragonal and *C*-centred orthorhombic unit cells (Table 3). However, the observation of unsplit peaks and the similarity between *a* and *b* when the pattern was indexed according to the orthorhombic cell may infer that the higher-symmetry tetragonal cell is more appropriate. Nevertheless, it is interesting that the lattice-plane spacings and unit-cell parameters for the material indexed according to a *C*-centred orthorhombic unit cell resemble those reported[5] for the material quenched from 900 °C: $a = 6.5289$, $b = 6.5061$, and $c = 3.0839$ Å. It seems, despite the larger proportion of Sb_2O_4 in the low-temperature material, that the two rutile-type phases formed at different temperatures are similar.

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