Structural Investigations of the Vanadium–Antimony–Oxygen System

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The structural properties and thermally induced behaviour of non-stoicheiometric vanadium antimonate and antimony tetroxide which are formed during solid-state reactions between antimony(III) oxide and vanadium(V) oxide in nitrogen have been investigated. The β-Sb_2O_4 phase which is formed at temperatures exceeding 800 °C as large hexagonal plate-type crystals is more accurately described as a solid solution of *ca.* 5% vanadium in β-Sb_2O_4. The formation of this ' β-Sb_2O_4 ' phase and the conversion of α- into β-Sb_2O_4 in the presence of vanadium at lower temperatures than those normally required for the transformation is associated with the incorporation of vanadium into the β-Sb_2O_4 structure. The oxidative decomposition of monophasic vanadium antimonate at temperatures exceeding 800 °C also gives ' β-Sb_2O_4 ' which, when subjected to continued thermolysis, generates an outgrowth of vanadium antimonate from the hexagonal crystalline faces. It is proposed that this results from the recombination of ' β-Sb_2O_4 ' with the vanadium(V) oxide formed in the initial reversible decomposition of vanadium antimonate.

As a result of considerable uncertainty in the literature[1-5] we, in the preceding paper[6] reported on the products which may be obtained from the solid-state reaction between antimony(III) oxide and vanadium(V) oxide. In particular we showed that monophasic vanadium antimonate may be prepared by slowly heating equimolar quantities of the reactants in strictly oxygen-free flowing nitrogen. The reaction in a limited supply of oxygen gave non-stoicheiometric vanadium antimonate of composition $VSb_{1-y}O_{4-2y}$ $(0 < y < 0.1)$ in the presence of antimony tetroxide. When performed in air the reaction gave oxidised materials of formula $V_{1-y}Sb_{1-y}O_4$ $(0 < y < 0.1)$. We report here on the structural properties of some of these phases, the changes induced by thermolysis, and the relationships between the various components in the system.

Experimental

Materials corresponding to the formulation $VSb_{1-y}O_{4-3/2y}$, or $VSb_{1-y}O_{4-2y}$ in the presence of Sb_2O_4 $(0 < y < 0.1)$, were prepared by methods previously described.[6]

X-Ray powder photographs were recorded with a Guinier de Wolff camera (diameter 228 mm) and diffraction data with a Philips vertical goniometer (PW 1050/70) using Cu-K_α radiation.

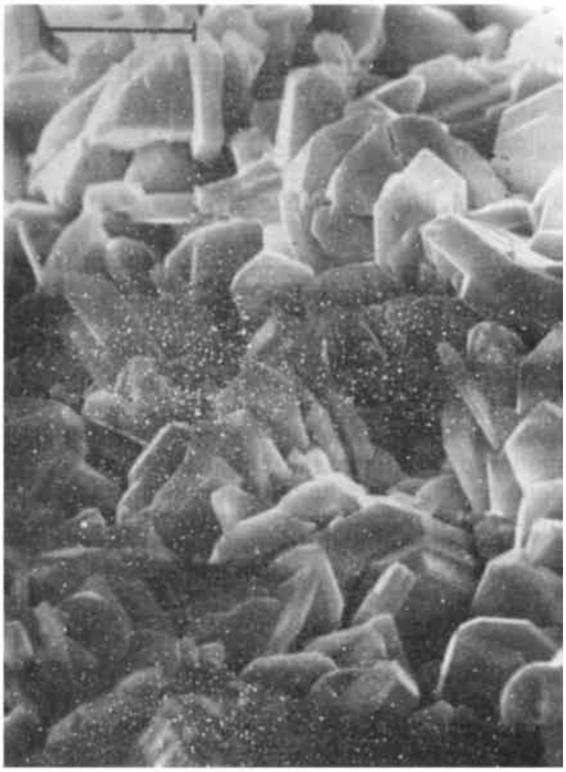
Scanning-electron microscopy was performed with Cambridge Stereoscan and JEOL JSM-35 instruments, transmission-electron microscopy with a Philips EM300 using the goniometer stage, and electron-probe microanalysis with an Ortec silicon-diode energy-dispersive *X*-ray detector interfaced with the EM300 or Stereoscan microscopes.

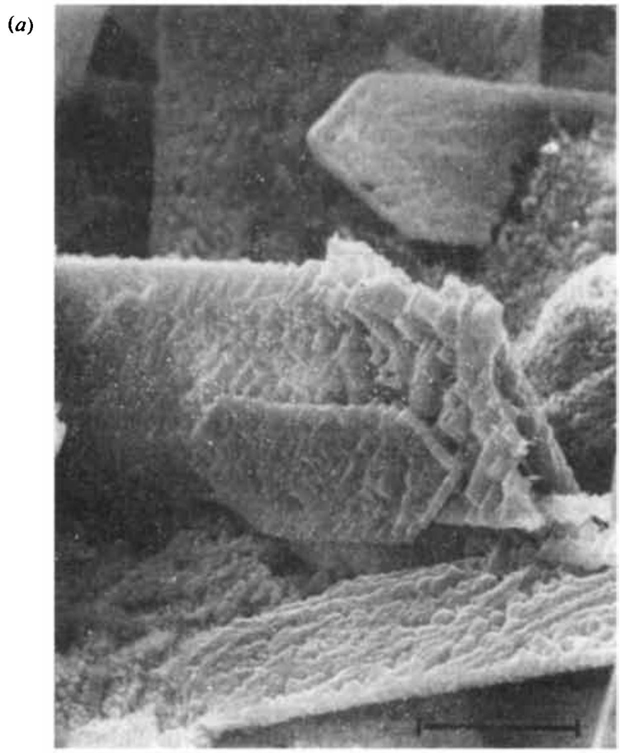
Results and Discussion

Although monophasic tetragonal rutile-type vanadium antimonate prepared[6] in oxygen-free nitrogen from reactions between antimony(III) oxide and vanadium(V) oxide gave *X*-ray diffraction patterns characteristic of a crystalline material, scanning-electron microscopy showed the absence of a well defined crystal habit. The antimony-deficient rutile-type materials obtained from similar reactions in nitrogen or sealed tubes[6] at temperatures below 800 °C were formed in the presence of cubic crystals of α-Sb_2O_4. These biphasic materials when heated in nitrogen to 900 °C and cooled slowly gave a fused product which supported fine needle-shaped crystals of up to *ca.* 1 mm in length with cell parameters $a = 12.1$, $b = 4.8$, and $c = 5.4$ Å, which are in good agreement with those attributed[7] to β-Sb_2O_4. Our previous work[6] has shown that early *X*-ray diffraction data from similar materials have sometimes been incorrectly interpreted and that evidence for the presence of antimony tetroxide has, on occasions, been ignored. The occurrence of β-Sb_2O_4 endorses our suggestion[6] that the additional species found in '$VSbO_4$' when the reaction mixture is quenched[2,5] from *ca.* 900 °C, previously described as a high-temperature polymorph[2] or a glassy antimony oxide,[5] is more accurately described as the high-temperature β form of antimony tetroxide. We also confirm that we remain unable to identify a species corresponding to that described[3] as $Sb_2V_2O_9$ which has been reported to result from the pyrolysis of '$VSbO_4$' in atmospheres containing oxygen.

The detection of β-Sb_2O_4 in these products was unexpected since direct oxidation of antimony(III) oxide produces[8,9] α-Sb_2O_4 which is isomerised[7] into the β form at 1 130 °C. Further experiments were therefore performed to investigate this low-temperature formation of β-Sb_2O_4 in the vanadium–antimony–oxygen ternary system.

The Low-temperature Formation of β-Sb_2O_4.—A mixture of antimony(III) oxide and vanadium(V) oxide with an Sb : V ratio of 18 : 1, when heated in nitrogen containing oxygen at 700 °C (24 h) and then in air at 810 °C (4 h), gave a black product containing large hexagonal plate-type crystals (Figure 1). Although the *X*-ray diffraction pattern indicated the crystals to be β-Sb_2O_4, chemical analysis by energy-dispersive analysis of the emitted *X*-rays revealed the presence of vanadium with Sb : V ratios of 20 : 1 being recorded from a general area of the sample at low magnification (× 500) and of 24 : 1 from one of the hexagonal plates. Given that we were unable to identify any oxides of vanadium in the product we propose that the β-Sb_2O_4 phase, which is usually formed as hexagonal plate-type crystals in the vanadium–antimony–oxygen system at temperatures exceeding *ca.* 800 °C, may be more accurately described as a solid solution of vanadium in β-Sb_2O_4. The extent of vanadium incorporation may be estimated from the observation that reaction mixtures containing a higher proportion of vanadium(V) oxide gave appreciable





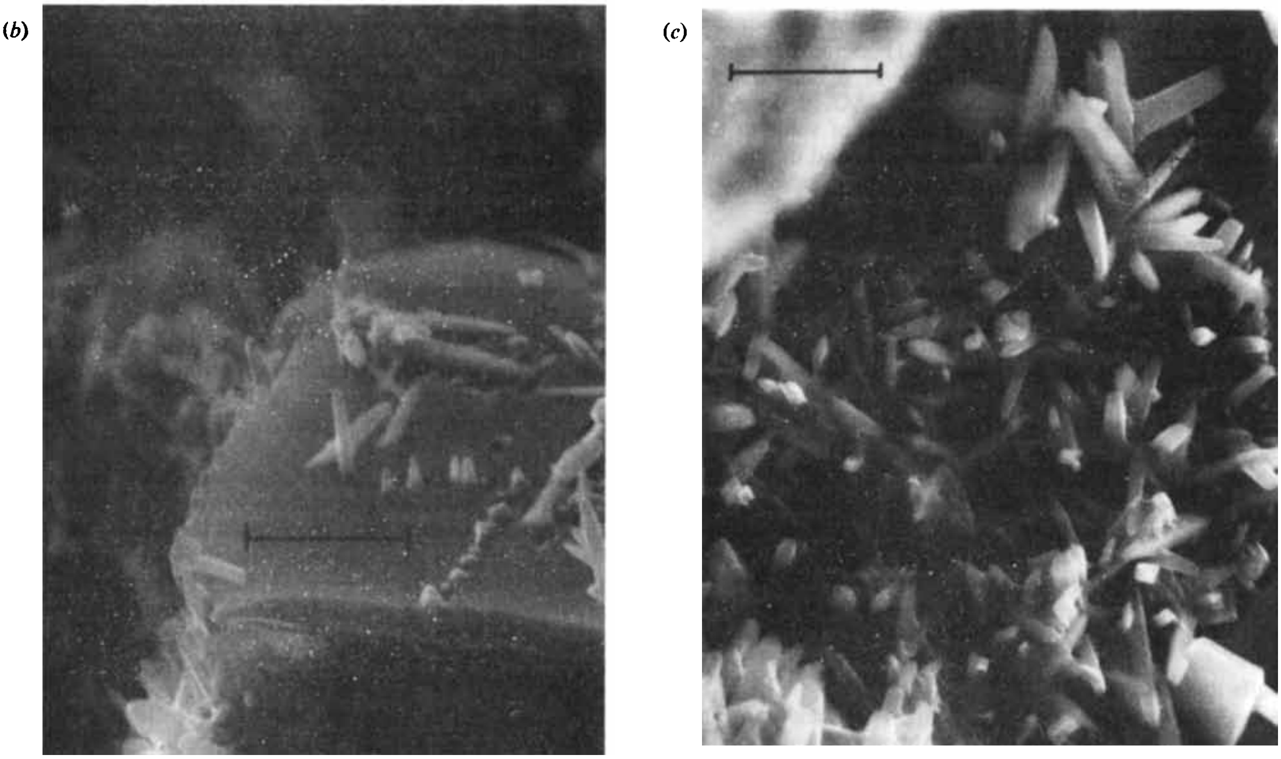
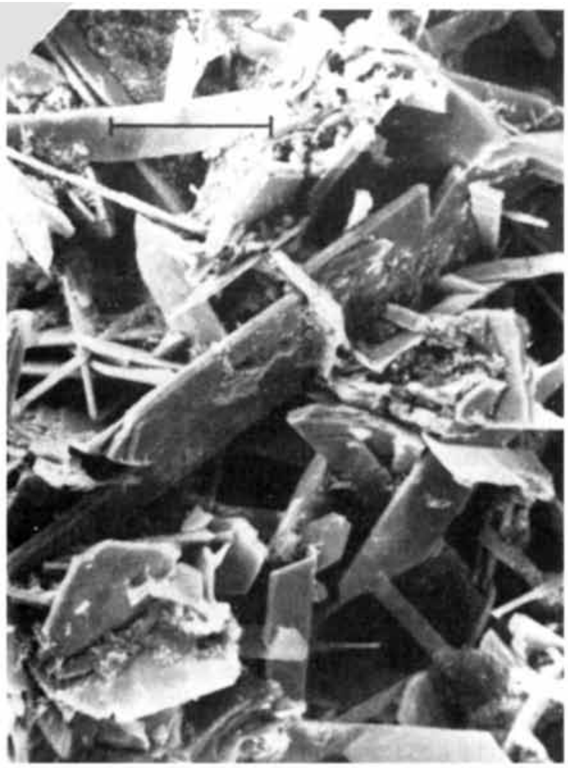
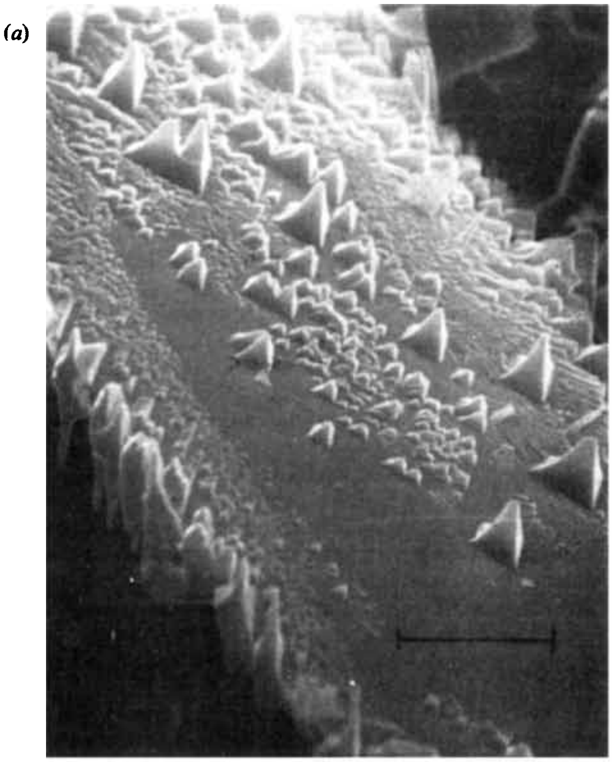
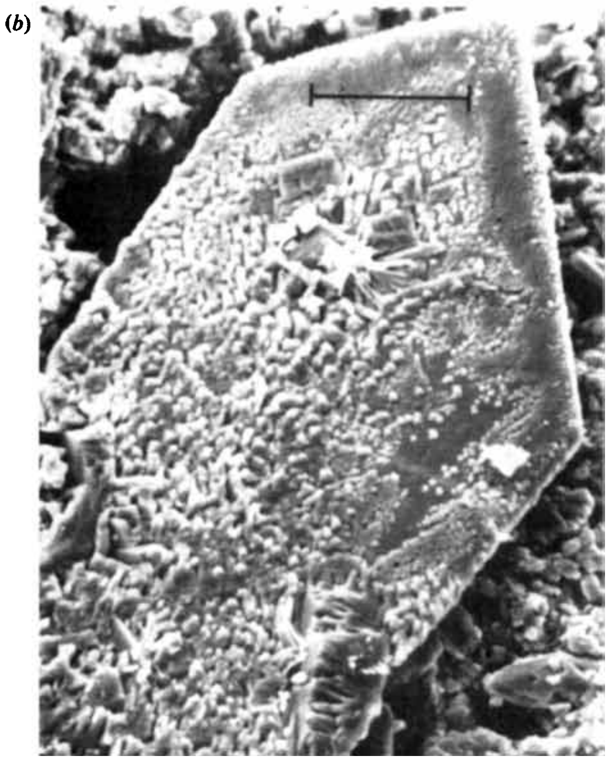


Figure 1. Hexagonal crystals of β-Sb_2O_4 containing *ca.* 5% vanadium formed from reaction of vanadium(v) oxide with antimony(III) oxide (scale bar = 10 μm)

Figure 2. Development of outgrowths from 'β-Sb_2O_4' formed by thermal decomposition of vanadium antimonate and subsequently heated at (*a*) 670 °C (27 h) (scale bar = 10 μm), (*b*) 810 °C (2.5 h), then 820 °C (7 h) (scale bar = 4 μm), and (*c*) 810 °C (6 h), then 848 °C (2.5 h) (scale bar = 4 μm)







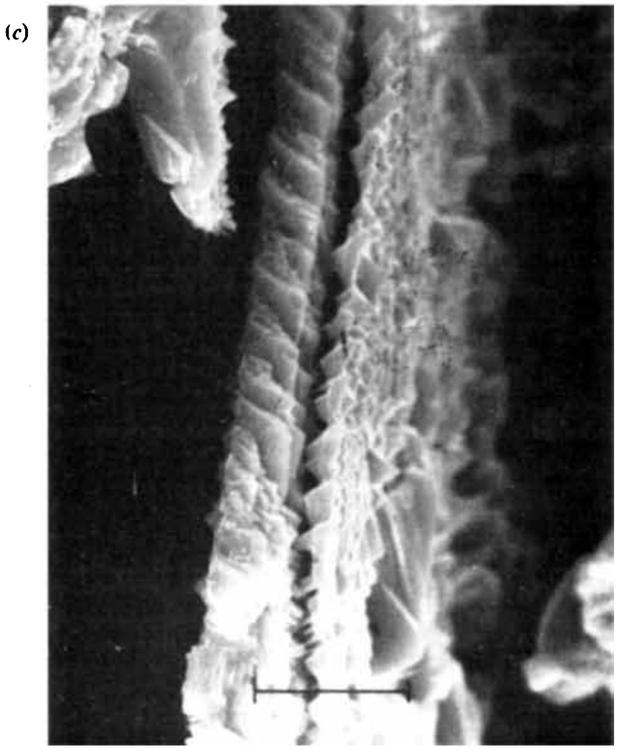


Figure 3. Hexagonal crystals of ' β-Sb_2O_4 ' formed from reaction of vanadium antimonate with antimony(III) oxide (scale bar = 40 μm)

Figure 4. Three stages (*a*)—(*c*) in the development of outgrowths from ' β-Sb_2O_4 ' following reaction with vanadium(V) oxide. Scale bar = 10 μm in (*a*) and (*c*), 40 μm in (*b*)

formation of an additional rutile-type phase corresponding to that reported [5,6] as $V_{1-y}Sb_{1-y}O_4$ or $VSb_{1-y}O_{4-2y}$ ($0 < y < 0.1$), whilst products from reaction mixtures containing less than 1 atom % vanadium in the form of vanadium(V) oxide gave *X*-ray diffraction patterns showing a mixture of α- and β-Sb_2O_4. Antimony(III) oxide when heated alone under the same conditions gave pure α-Sb_2O_4. It seems therefore that the presence of vanadium confers the β structure on the antimony tetroxide over quite a narrow composition range and that the limit of vanadium solubility in the β form of antimony tetroxide is *ca.* 5 atom %. Whether or not this involves the replacement of some octahedrally co-ordinated antimony(V) ($r = 0.60$ Å) [10] in antimony tetroxide by vanadium(V) ($r = 0.54$ Å) [10] is currently unclear.

We also found that α-Sb_2O_4 when heated at 810 °C for 12 h with vanadium(V) oxide (Sb : V = 20 : 1) in nitrogen was transformed to 'β-Sb_2O_4' with some vanadium antimonate appearing as a minor product. The conversion of α- into β-Sb_2O_4 is normally achieved at 1 130 °C by a mechanism which has been described [7] in terms of the dissociation of α-Sb_2O_4 into gaseous Sb_2O_3 which recombines with oxygen and condenses as β-Sb_2O_4. It would seem from the results reported here that vanadium facilitates and stabilises the formation of β-Sb_2O_4 from the α phase by a lower-temperature process which involves the incorporation of vanadium in the antimony tetroxide structure. Comparisons of these products with those formed during similar experiments at 750 °C show that the lower-temperature limit of *ca.* 800 °C for moderately short thermal treatments is quite well defined. Since the results of our experiments above this temperature suggested the existence of a special relationship between the separate components of the antimony–vanadium–oxygen ternary system we conducted further investigations in an attempt to elucidate the effects of calcination on vanadium antimonate and the solid solution of vanadium in β-Sb_2O_4.

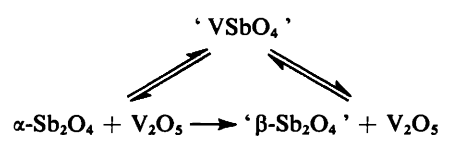
Annealing of '$VSbO_4$' *and* 'β-Sb_2O_4'.—*X*-Ray diffraction showed that calcination of monophasic vanadium antimonate at 810 °C (3 h) in air gave partial decomposition into approximately equal proportions of α- and β-antimony tetroxide. However, after calcination for 11 h, the antimony tetroxide was present only in the form of the β polymorph. Additional heat treatment resulted in the formation of crystal outgrowths from the β-Sb_2O_4 hexagonal faces with the type of outgrowth depending on the calcination temperature. For example, prolonged calcination at 670 °C (27 h) gave platelets as shown in Figure 2(*a*), whereas clusters of needle-shaped outgrowths were observed at higher temperatures [Figure 2(*b*) and (*c*)] in materials shown by *X*-ray diffraction to contain vanadium antimonate, β-Sb_2O_4, and a small amount of vanadium(V) oxide. Electron-probe microanalysis showed the needle-shaped crystals to contain approximately equal proportions of vanadium and antimony as might be expected in an outgrowth of a vanadium antimonate phase.

The results of these investigations suggested that the cationic species within the separate components were susceptible to thermally induced mobility. Further experiments were therefore performed to examine the nature of the products resulting from such cation migration.

Reaction of '$VSbO_4$' *with Antimony*(III) *Oxide*.—Heating monophasic vanadium antimonate with 10% antimony(III) oxide at 500 °C (2 h) in air resulted in oxidation of Sb_2O_3 to α-Sb_2O_4 which was converted into the β form at 810 °C (1.5 h). Prolonged heating (11 h) at this temperature gave a product of similar morphology (Figure 3) to that observed when monophasic vanadium antimonate was heated under similar conditions, except that the sample showed a higher proportion of the hexagonal 'β-Sb_2O_4' plate-like crystals as a result of antimony(III) oxide in the initial reaction mixture.

Reaction of 'β-Sb_2O_4' *with Vanadium*(V) *Oxide*.—A mixture of β-Sb_2O_4 containing 5% vanadium and vanadium(V) oxide corresponding to the overall stoicheiometry of $VSbO_4$ gave, after heating at 750 °C for 4 h in air, a product which was shown by *X*-ray diffraction to contain rutile-type vanadium antimonate with traces of vanadium(V) oxide and β-Sb_2O_4. The reaction therefore appears to reach virtual completion after only moderate heat treatment. Scanning-electron microscopy revealed an outgrowth of crystals from the 'β-Sb_2O_4' platelet surfaces. Although samples calcinated at only one temperature, *e.g.* 650 (13), 800 (15), 820 (3.5), or 820 °C (18.5 h), appeared as an amorphous-looking overlayer on the platelet surface, more well defined crystalline outgrowths of an irregular cubic structure were formed in predominance when the samples were thermally worked up. For example, the crystalline outgrowths resulting from sequential calcination at 650 (13), 750 (10.5 h), 800 (15), and finally 820 °C (18.5 h) are shown in Figure 4(*a*). Fully developed crystals achieved when the last two stages involved calcination at 800 °C for 1 h followed by 820 °C (18.5 h) are shown in Figure 4(*b*) and (*c*). Since the *X*-ray diffraction patterns from these materials showed only the presence of β-Sb_2O_4 and vanadium antimonate we deduce that the outgrowth is representative of the vanadium antimonate phase.

The fully developed outgrowths are very similar to those observed when the 'β-Sb_2O_4' crystals formed by calcination of vanadium antimonate were heated [Figure 2(*a*)]. Indeed, the edge-on view of an equilibrated platelet [Figure 4(*c*)] shows the outgrowth of parallel layers of vanadium antimonate from the opposing hexagonal faces of the platelet and this feature, common to all fully reacted β-Sb_2O_4 platelets, appears to be characteristic of the development of this phase. Given that these outgrowths of vanadium antimonate [Figure 4(*c*)] resulted from the reaction between vanadium(V) oxide and vanadium-containing β-Sb_2O_4 and since similar structures appeared when 'β-Sb_2O_4' was heated with vanadium antimonate, it seems reasonable that the outgrowth shown in Figure 2(*a*) occurs by a related process. Hence, we propose that calcination induces the reversible oxidative decomposition of vanadium antimonate to vanadium(V) oxide and α-Sb_2O_4 and that further reaction occurs in which some of the V_2O_5 dissolves in the α-Sb_2O_4 with concurrent isomerisation of the structure to the β form. Thereafter, antimony in the 'β-Sb_2O_4' platelet crystal migrates away from the surface to recombine with remaining V_2O_5 to yield an outgrowth of vanadium antimonate as shown below. The mechanism is



supported by the conversion of α-Sb_2O_4 into the β polymorph and some vanadium antimonate when heated at 810 °C with vanadium(V) oxide.

Acknowledgements

The authors thank Dr. R. T. Murray of ICI Corporate Laboratory for microscopy and the S.E.R.C. for a studentship (to M. E. B.).

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Received 4th May 1982; *Paper* 2/721