

## Formation of Vanadium Antimonate and Low Temperature Stabilisation of $\beta$ - $\text{Sb}_2\text{O}_4$ by Vanadium

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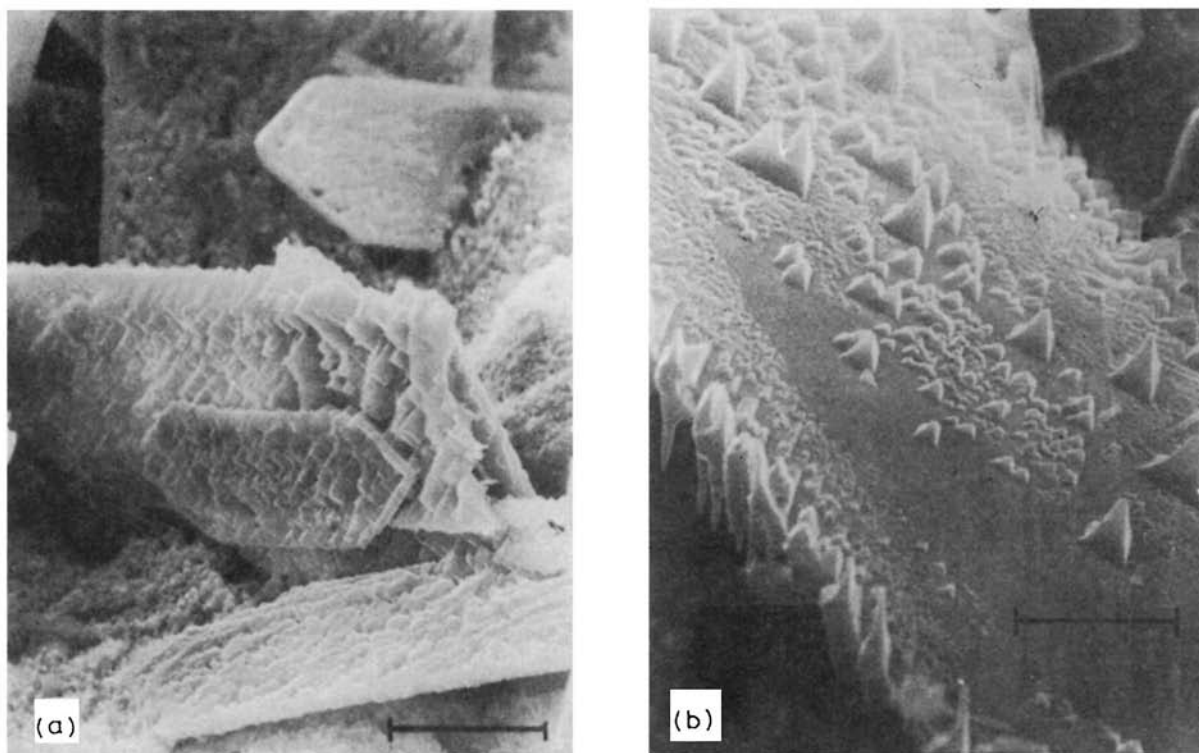
The formation of hitherto disputed monophasic vanadium antimonate is reported and its thermally induced decomposition into  $\beta$ - $\text{Sb}_2\text{O}_4$  containing ca. 5% vanadium is associated with a new low-temperature stabilisation of this phase; on further heating the hexagonal ' $\beta$ - $\text{Sb}_2\text{O}_4$ ' plate-type crystals develop crystalline outgrowths of vanadium antimonate.

The preparation of a compound with formula  $\text{VSbO}_4$  from the solid state reaction between antimony(III) oxide and vanadium(V) oxide has been the subject of considerable uncertainty<sup>1-5</sup> and doubt has recently<sup>6</sup> been cast on the formation of monophasic vanadium antimonate.

We have prepared monophasic vanadium antimonate by slowly and carefully heating intimately ground equimolar mixtures of the reactants to 750 °C in a flow of dry nitrogen from which oxygen has been removed by manganese(II) oxide (<ca. 1 part in 10<sup>9</sup>).<sup>6</sup> X-Ray diffraction and electron microscopy studies showed the absence of antimony tetroxide in the product which gave an X-ray diffraction pattern characteristic of a tetragonal rutile-type material with cell parameters  $a = b = 4.600 \pm 0.004$ ,  $c = 3.078 \pm 0.004$  Å. The reaction was accompanied by the sublimation of white crystalline cubic antimony(III) oxide suggesting that although monophasic the vanadium antimonate may nevertheless be non-stoichiometric and correspond to the formulation  $\text{VSb}_{1-y}\text{O}_{4-3/2y}$  ( $0 < y < 0.1$ ). Preparations under identical conditions but without the removal of residual oxygen from the nitrogen by manganese(II) oxide gave biphasic products consisting of rutile-type vanadium antimonate and  $\alpha$ - $\text{Sb}_2\text{O}_4$ . Above 800 °C

the  $\text{Sb}_2\text{O}_4$  was formed as the  $\beta$ -polymorph. The quantity of antimony tetroxide formed in these products exceeded that which might reasonably be attributed to the oxidation of reactant antimony(III) oxide by residual molecular oxygen in the impure nitrogen flow gas. We suggest that initial oxidation of antimony(III) oxide by the residual oxygen gives  $\alpha$ - $\text{Sb}_2\text{O}_4$  which liberates oxygen from vanadium(V) oxide by a similar mechanism to that which has been suggested for the reaction between vanadium(V) oxide and metal oxides.<sup>7-9</sup> Hence further oxidation of unchanged antimony(III) oxide gives rise to larger amounts of  $\text{Sb}_2\text{O}_4$  in products which show minimum weight gain. Reactions of antimony(III) oxide and vanadium(V) oxide in air gave single phase homogeneous oxidised products. We have been unable to confirm the existence<sup>3</sup> of a compound of formula  $\text{V}_2\text{Sb}_2\text{O}_9$ . We suggest that the method by which monophasic vanadium antimonate is prepared may be suitable for the synthesis of similar compounds with related structures which are not usually formed<sup>10</sup> without an oxide impurity.

The biphasic product containing vanadium antimonate and  $\alpha$ - $\text{Sb}_2\text{O}_4$  gave, when heated to 900 °C and slowly cooled, a fused product supporting crystals with cell parameters  $a =$



**Figure 1.** Outgrowths from ' $\beta$ - $\text{Sb}_2\text{O}_4$ ' (a) formed by thermal decomposition of vanadium antimonate with subsequent heating at 670 °C (27 h) (Scale bar = 10  $\mu\text{m}$ ); (b) following reaction with vanadium(V) oxide at 650 °C (13 h) and sequentially heated at 750 °C (10.5 h), 800 °C (15 h), and 820 °C (18.5 h) (Scale bar = 10  $\mu\text{m}$ ).

12.1,  $b = 4.8$ , and  $c = 5.4 \text{ \AA}$ , similar to those reported<sup>11</sup> for  $\beta\text{-Sb}_2\text{O}_4$ . The formation of  $\beta\text{-Sb}_2\text{O}_4$  under these conditions, and from reactions between vanadium(v) oxide and either antimony(III) oxide or  $\alpha\text{-Sb}_2\text{O}_4$  in impure nitrogen at temperatures exceeding  $800^\circ\text{C}$ , is unexpected since direct oxidation of antimony(III) oxide produces<sup>12,13</sup>  $\alpha\text{-Sb}_2\text{O}_4$  which is converted into the  $\beta$ -form at  $1130^\circ\text{C}$ .<sup>11</sup> Further reactions between antimony(III) oxide and vanadium(v) oxide with V:Sb ratios between 1:18 and 1:100 gave black products containing large hexagonal plate-type crystals which  $X$ -ray diffraction showed to be  $\beta\text{-Sb}_2\text{O}_4$ . Reaction mixtures with vanadium contents outside these limits gave biphasic products in which the  $\beta\text{-Sb}_2\text{O}_4$  was accompanied by rutile-type vanadium antimonate in vanadium rich reactions or  $\alpha\text{-Sb}_2\text{O}_4$  in vanadium deficient systems. Chemical analysis of the  $\beta\text{-Sb}_2\text{O}_4$  plates by electron probe microanalysis revealed the presence of up to ca. 5% vanadium. We therefore propose that the ' $\beta\text{-Sb}_2\text{O}_4$ ' phase is more accurately described as a solid solution of vanadium in  $\beta\text{-Sb}_2\text{O}_4$  and that the vanadium facilitates and stabilises the low temperature formation of  $\beta\text{-Sb}_2\text{O}_4$ .

It is to be expected that the low temperature transformation of  $\alpha$ - to ' $\beta\text{-Sb}_2\text{O}_4$ ' occurs by a different mechanism from that which has been proposed<sup>11</sup> for the isomerisation of pure  $\alpha\text{-Sb}_2\text{O}_4$  at  $1130^\circ\text{C}$ . In this respect it is significant that calcination of monophasic vanadium antimonate at  $810^\circ\text{C}$  (11 h) also gave the formation of the ' $\beta\text{-Sb}_2\text{O}_4$ ' crystals which on subsequent heating at  $670^\circ\text{C}$  (27 h), or at higher temperatures, developed [Figure 1(a)] crystalline outgrowths from the hexagonal faces in materials shown by  $X$ -ray diffraction to contain vanadium antimonate,  $\beta\text{-Sb}_2\text{O}_4$  and a small amount of vanadium(v) oxide. Electron probe microanalysis showed the outgrowths to contain approximately equal proportions of antimony and vanadium as might be expected from a vanadium antimonate phase. Similar products [Figure 1(b)] were obtained when mixtures of  $\beta\text{-Sb}_2\text{O}_4$  containing 5% vanadium and vanadium(v) oxide corresponding to the overall stoichiometry  $\text{VSbO}_4$  were heated at  $650^\circ\text{C}$  (13 h) and then thermally worked up. The detection by  $X$ -ray diffraction of both  $\beta\text{-Sb}_2\text{O}_4$  and vanadium antimonate in these materials is indicative of an outgrowth of vanadium antimonate resulting from the reaction of vanadium(v) oxide with the hexagonal ' $\beta\text{-Sb}_2\text{O}_4$ ' platelet faces. It is not unreasonable therefore to suggest that

the outgrowth formed on the ' $\beta\text{-Sb}_2\text{O}_4$ ,' generated by calcination of monophasic vanadium antimonate, is derived in a similar fashion. We therefore propose that calcination induces the decomposition of vanadium antimonate into vanadium(v) oxide and  $\alpha\text{-Sb}_2\text{O}_4$  and that further reaction occurs in which some vanadium from the vanadium(v) oxide dissolves in the  $\alpha\text{-Sb}_2\text{O}_4$  lattice with concurrent isomerisation to the  $\beta$ -form. Thereafter the remaining vanadium(v) oxide slowly recombines with the  $\beta\text{-Sb}_2\text{O}_4$  losing oxygen to yield an outgrowth of vanadium antimonate. In view of the mobility which has been attributed<sup>14</sup> to antimony in other rutile-type structures it appears reasonable to suggest that the migration of such species to surface sites and their nucleation to form macroscopically distinguishable phases is a more common consequence of thermolysis of these structures than is generally realised.

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