SINGLE CRYSTAL TRANSFORMATION OF ORTHORHOMBIC Sb_2O_3 TO ORTHORHOMBIC Sb_2O_4

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ABSTRACT

The transformation of orthorhombic Sb_2O_3, valentinite, to orthorhombic Sb_2O_4, cervantite has been studied by single crystal X-ray diffraction techniques. The reaction has been found to be topotactic. The orientation relationships and the similarity of the two structures have been established.

ANTIMONY TRIOXIDE (Sb_2O_3) exists in two crystalline forms, the low temperature cubic senarmontite and the high temperature orthorhombic valentinite, with a transition temperature of approximately 573° C.[1] Antimony tetroxide (Sb_2O_4) has also been found to exhibit polymorphism. Apart from the orthorhombic form, cervantite,[2] a high temperature monoclinic variety has also recently been identified.[3] Sb_2O_4 can be obtained by the oxidation of Sb_2O_3 in air.[4] However, no detailed structural studies on the conversion have been reported. We have studied the transformation of valentinite to cervantite by single crystal X-ray diffraction techniques, established the orientation relationships between the two and deduced their structural similarity, which we report here.

The structure of valentinite, determined by Buerger,[5] is composed of infinitely long chains of Sb_4O_6 groups, alternate chains in the unit cell running antiparallel. Within the chain each antimony is linked to 3 oxygens and each oxygen to 2 antimony atoms. The chains are held together in the crystal by secondary weak Sb-O bonds. The structure of cervantite has not been determined so far for lack of suitable single crystals.[3] However, the structure of isostructural $SbNbO_4$ has recently been established by Skapski and Rogers.[6] Prof. Rogers has kindly sent us the atomic co-ordinates for $SbNbO_4$ prior to publication[7] and we have used these in the following discussion. The cell dimensions for Sb_2O_4 as well as Sb_2O_3 have been taken from N.B.S. data.[8] Sb_2O_4 is actually $Sb^{III}Sb^{V}O_4$ and its structure consists of corrugated sheets of $Sb^{V} - O$ octahedra linked by sharing corners and running parallel to (010).[8] Adjacent sheets of these octahedra are joined by Sb^{III} atoms which are thus bonded

to 4 oxygen atoms. Crystallographic data for the two oxides are tabulated in Table I.

TABLE I

Crystallographic data for valentinite and cervantite

	Valentinite, Sb_2O_3	Cervantite, Sb_2O_4*
a	4·914 Å	4·810 Å
b	12·468 Å	11·76 Å
c	5·421 Å	5·436 Å
Z	4	4
Space group	Pccn	Pc2$_1$n

Single crystals of valentinite, of size suitable for X-ray work, were prepared by heating Sb_2O_3 powder of semiconductor purity at 630° C., *i.e.*, just below its melting point, in a platinum container placed inside a sealed pyrex glass tube. Crystals of valentinite were converted into cervantite by heating in the presence of air in a tubular furnace at temperatures around 490° C. for different intervals of time. The crystals were then air-quenched and examined by X-ray rotation and Weissenberg techniques. These photographs reveal spots corresponding to interpenetrating reciprocal lattices of valentinite and cervantite, indicating that a crystal of valentinite which is incompletely oxidised gives a 'hybrid' crystal of the two oxides. With increased time of oxidation the amount of cervantite in the hybrid increases and finally pure cervantite crystals are obtained. At 490° C., the transformation was complete in about 8 hours. Analysis of the photographs of the hybrid crystal shows that the crystallographic axes a, b and c of valentinite (v) are respectively transformed into the a, b and c axes of cervantite (c). The following orientation relationships are thus established:

$$[100]_v \parallel [100]_c$$
$$[010]_v \parallel [010]_c$$
$$[001]_v \parallel [001]_c$$

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* The crystallographic axes of Skapski and Rogers have been interchanged to facilitate comparison with Sb_2O_3.

It is now of interest to compare the two structures, keeping in view the experimental result that the individual axes are parallel. Two projections of the valentinite and cervantite structures along [100] and [001] are shown left and right respectively in Figs. 1 and 2. In both projections one can

Sb(3) also form additional bonds to oxygens O(2') and O(9') respectively of a neighbouring anti-parallel chain, these being the secondary weak bonds described by Buerger in valentinite. As a result Sb(1) and Sb(3) acquire a distorted octahedral co-ordination. The contraction in a and b dimensions as a result of the
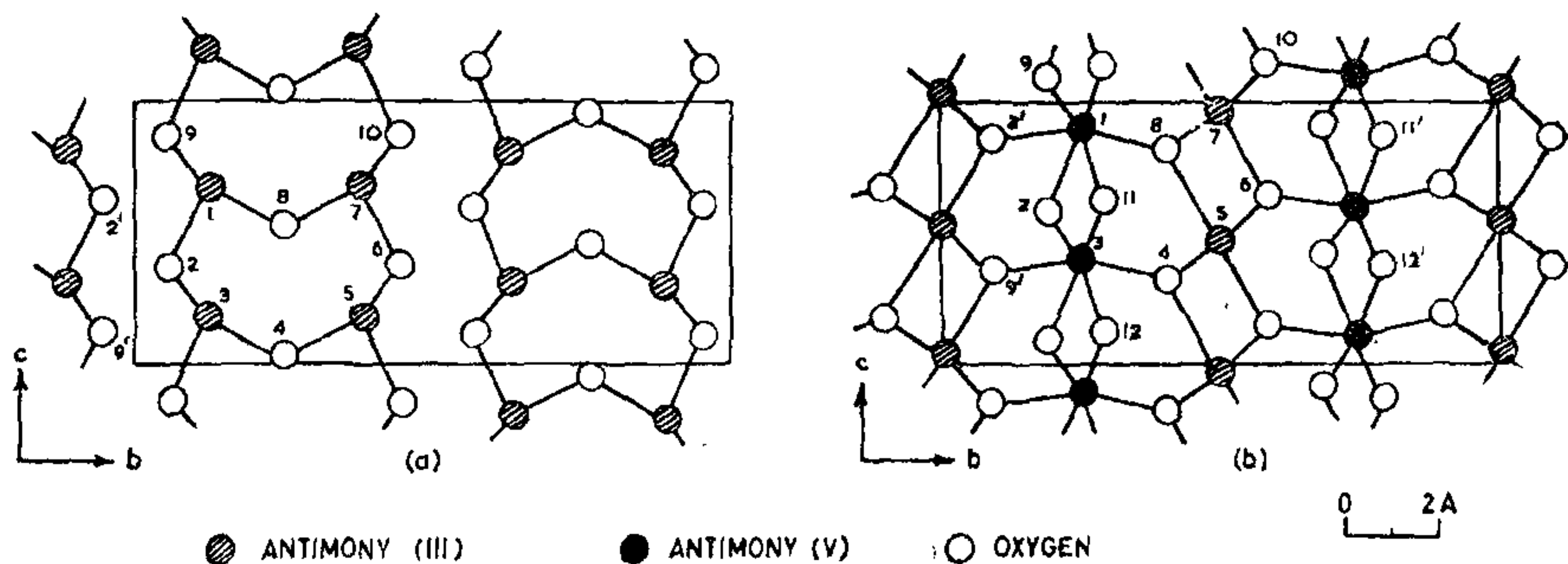

ⓧ ANTIMONY (III)   ● ANTIMONY (V)   ○ OXYGEN

FIG. 1. Structures of valentinite (*a*) and cervantite (*b*) projected along [100].

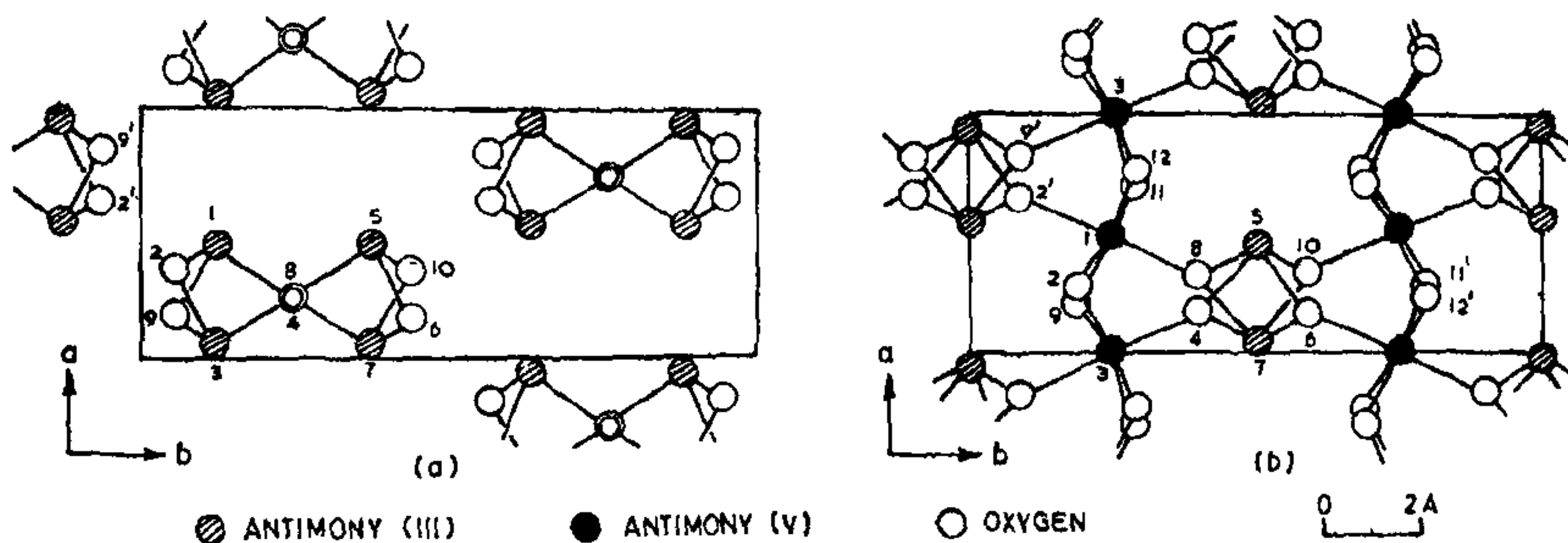ⓧ ANTIMONY (III)   ● ANTIMONY (V)   ○ OXYGEN   0   2A

FIG. 2. Structures of valentinites (*a*) and cervantite (*b*) projected along [001].

identify the Sb_4O_6 group corresponding to valentinite and designated Sb(1) O(2) Sb(3) O(4) Sb(5) O(6) Sb(7) O(8) O(9) O(10) in cervantite. It is therefore evident that the relative positions of atoms in valentinite are more or less preserved in cervantite. The only two additional atoms in the latter are O(11) and O(12). As the [001] projection clearly shows, the valentinite structure has channels between the $(Sb_4O_6)_\alpha$ chains parallel to the c axis and these additional oxygen atoms occupy positions along these channels close to the antimony atoms. Each oxygen links up two antimony atoms of neighbouring chains along [100]. For example O(11) bonds with Sb(1) and Sb(3) and O(12) with Sb(3) and Sb(1) of the neighbouring cell. Sb(1) and

transformation is easily understood on the basis of a closing up of the chains along these directions. The conversion of the chain structure of valentinite into the three-dimensional structure of cervantite also follows from the above arguments. Exactly similar changes take place in the other half of the unit cell because of the two extra oxygen atoms O(11') and O(12').

In view of the close structural relationship in three dimensions between valentinite and cervantite, this transformation is obviously a topotactic reaction.[9-11] A more detailed understanding of the mechanism of this transformation should await the results of kinetic and optical studies and the crystal structure analysis of cervantite which are being undertaken.

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SCAVENGING OF NUCLEAR FISSION PRODUCTS BY SEAWEEDS FROM SEA-WATER

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LIFE has developed on earth in conditions of continual exposure to low levels of ionizing radiations referred to as natural radioactivity. But with the advent and utilization of nuclear energy for peaceful purposes and the increasing use of radionuclides and ionizing radiations in scientific research, in industry, medicine and agriculture involving the production of large amounts of radioactive waste, there arises a new parameter namely the determination of the extent of harmful effects of the above factors on man and elimination of this effect. The removal of radioactive fission fragments and waste material from the contaminated sea-water, area and species has been a problem and so far, the techniques used involve complexing with chemical reagents like EDTA.[1] It is known[2,3] that certain seaweeds have a specific capability to concentrate various trace elements and it is now thought to profitably use the seaweeds as scavengers of contaminated radioactivity since their removal from the medium is simple. A successful method for the removal of radioactive fission fragments Sr^{90}, Cs^{137}, Ru^{106}, I^{131} and Zn^{65} (waste product) from contaminated sea-water specially meant for desalination and drinking purposes, using marine and freshwater algæ has been tried and is described below.

A stock solution of filtered sea-water containing about $0.02 \mu c./l$. (500–600 cpm./ml.) of the respective radionuclide (Sr^{90}, Cs^{137},

Ru^{106}, I^{131} and Zn^{65}) was prepared for the scavenging experiments. To fifty millilitres of the above sea-water one gram of fresh algal material, collected from Okha and Veraval coasts, was added after it was washed with tap-water and blotted dry. In some cases, ten gram of algal material was taken in 500 ml. of sea-water. A couple of samples were kept in dark while others were exposed to direct sunlight (Ca 3375 ft. candles) for 30, 60 and 120 minutes. The algal sample (W) was immediately removed, washed with alcohol, dried at 105° C., powdered and counted. The left over (A') and original (A) radioactivities in sea-water was measured by pipetting out 1 ml. (W') of it into a plastic tube (γ–) or S.S. planchet (β—4·91 sq. cm.) and counted for γ-activity in a GRS 20 B, γ-ray spectrometer (ECI) and β-activity with a F.H. 90 scaler. From the data thus obtained, the percentage activity scavenged by each seaweed was calculated as

$$\% S = W(A - A')/W'A \cdot 100$$

Practically all the available marine algæ of the west coast were tried and the effect of temperature, pH and light on scavenging were also studied.

It is seen from Table I that about 50% of the activity can be removed from contaminated sea-water by selecting the appropriate algal species for each of the radionuclides. Thus,