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# An Electron Microscope Study of Tin Dioxide and Antimony-Doped Tin Dioxide

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Crystals of tin dioxide, $SnO_2$, have been grown pure or doped with a few percent of antimony using vapor growth methods in order to investigate the microstructures of reduced and oxidized $SnO_2$. They were examined by X-ray diffraction and by optical and electron microscopy. $SnO_2$ crystals were found to contain few faults, but the antimony-doped crystals were extensively twinned in some regions. Reduction of $SnO_2$ crystals to yield *CS* phases was unsuccessful. These results are discussed in terms of the known crystal chemistry of the oxides involved.

## Introduction

Although about twenty oxides are known which adopt the rutile structure type (*1*), only two of these are fully oxidized and stable under normal conditions of temperature and pressure, namely $TiO_2$, rutile, and $SnO_2$, cassiterite. The electrical and catalytic properties of pure and doped $SnO_2$ have been well studied because of applications in semiconducting devices and the industrial use of catalysts formed from the ternary Sb–Sn–O system. Similarly some physical properties of $TiO_2$ and its catalytic and photochemical behavior are well studied. However, while the crystal chemistry of $TiO_2$ and reduced or doped rutile is well known the crystal chemistry of reduced and doped $SnO_2$ has received little attention. The present study attempts to rectify, at least in part, this situation.

Reduction of $TiO_2$ leads to an extensive series of crystallographic shear (*CS*) phases (*2*), as does doping with Cr (*2*) and Fe (*3*), while doping with Ga leads to a complex series of intergrowth phases (*4*). In general, therefore, structural studies have indicated that stoichiometric imbalance in $TiO_2$ is not accommodated to any appreciable extent by the formation of point defects, but rather by the formation of planar faults. As $SnO_2$ so closely parallels $TiO_2$ in many respects, it is of interest to determine whether $SnO_2$ is also intolerant of point defect formation. This paper describes the results of a study of $SnO_2$, reduced $SnO_2$, and $SnO_2$ doped with antimony. In general it was found that $SnO_2$ does not form *CS* phases and appears to be more tolerant of a point defect population than $TiO_2$ although the presence of antimony does lead to extensive twinning of the $SnO_2$ matrix. These results are discussed in terms of the known chemical and physical properties of the rutile-type oxides.

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## Experimental

Crystals of pure $SnO_2$ and $SnO_2$ doped with antimony have been prepared by vapor phase deposition starting from both the chloride(s) and the pure metal(s). The chloride method used a vapor phase reaction between $SnCl_4$ and water vapor carried in nitrogen streams and mixed in a hot tube as described by Nagasawa *et al.* (*5*). This gave crystals of pure $SnO_2$ which were formed at 1273 to 1373°K. The inclusion of $SbCl_5$ in the $SnCl_4$ stream produced doped crystals at similar temperatures. The method described by Morgan and Wright (*6*) was employed to prepare crystals from the metal(s). In this technique, tin vapor formed in passing argon over the powdered metal at 1673°K was reacted with oxygen at 1723°K to deposit crystals of $SnO_2$. Doping with antimony was achieved by mixing in antimony vapor from the metal held at 873 to 973°K, the extent of doping being controlled by the temperature of the antimony metal.

Reduction of the pure $SnO_2$ crystals was attempted by sealing them in silica ampoules together with sufficient Sn metal to yield an overall stoichiometry of between $SnO_{1.8}$ and $SnO_{1.9}$ and heating at 1073°K or higher. In addition reduction by flowing hydrogen gas at 873°K was also attempted.

The crystals were examined optically using a Zeiss Ultraphot optical microscope, and selected samples were studied further using a JEM 100B electron microscope fitted with a goniometer stage and operated at 100 kV. Electron microscope samples were prepared by crushing the crystals under *n*-butanol in an agate mortar and allowing a drop of the resultant suspension to dry on a netlike carbon support film. Only those fragments projecting over holes in the film were examined.

Powder X-ray diffraction photographs were taken of some crystals using a Guinier–Hägg focusing camera employing strictly monochromatic $CuK\alpha_1$ radiation and KCl ($a_0 = 0.62923$ nm) as an internal standard. Lattice parameters were refined by least-squares techniques using a program provided by Werner (*7*).

Crystals were analyzed by quantitative X-ray fluorescence analyses.

## Results and Interpretation

### *$SnO_2$ and Reduced $SnO_2$*

$SnO_2$ crystals prepared by the chloride method described above grew on the silica tubes which conducted the reacting gases into the furnace and on the mullite furnace tubes. Some of these latter crystals were discolored where they were in contact with the mullite but the majority were transparent and colorless. The habits of the crystals varied and usually clusters grew with a tabular habit, but dendritic growth was also found on occasion, suggesting that a more critical control of furnace temperature and flow rates of reactants are needed to achieve large perfect single crystals (*5*, *8*). For our purposes the crystal clusters were adequate and large crystals of 1 to 2 mm could usually be separated manually. Typical crystals are shown in Fig. 1a. The preparation from tin metal gave fine needlelike crystals up to 10 × 0.5 mm shown in Fig. 1b. The difference in habit between the two preparation methods may be due to the different growth temperatures employed (*10*, *13*).

Powder X-ray diffraction patterns of the crushed crystals were in good agreement with the literature data for $SnO_2$ as were the values of the lattice parameter found, viz., $a = 0.4736$ nm, $c = 0.3185$ nm (*9*). These values did not vary significantly from sample to sample.

Examination of these crystals by electron microscopy showed that the crystal fragments were uniform in appearance. The faulting present was limited to dislocations and features that could be attributed to fracture damage. No planar faults or precipitates were observed.

The attempted reduction of $SnO_2$ using sealed tubes or hydrogen was totally unsuccessful, the crystals remaining clear and to

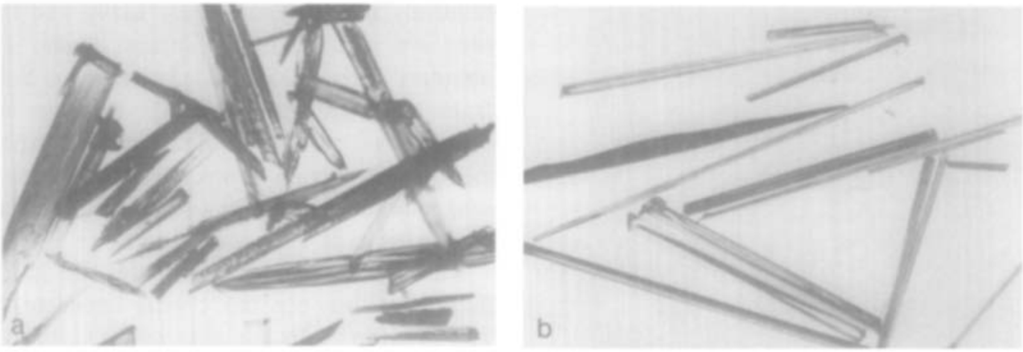

FIG. 1. (a) Crystals of $SnO_2$ grown from $SnCl_4$ vapor at 1273–1373°K, (b) crystals of $SnO_2$ grown from metal vapor and oxygen at 1723°K. Magnification of prints 7×.

all intents and purposes unchanged although a dark discoloration, possibly Sn or SnO, was sometimes noted on the surfaces of some fragments. The X-ray powder pattern was identical to the as grown crystals in intensity and the lattice parameters were also identical. Electron microscope examination was unable to reveal any changes with respect to the starting material. In particular no *CS* planes were observed.

### *$SnO_2$ Doped with Antimony*

Both techniques for preparing $SnO_2$ crystals doped with antimony led to the production of deep blue crystals. On the whole crystal habit was similar to that for the binary $SnO_2$ crystals shown in Fig. 1 and dendrites were again occasionally observed. Powder X-ray diffraction revealed that the crystals showed only lines due to $SnO_2$ and that the lattice parameters, $a = 0.4732$ nm, $c = 0.3185$ nm were not significantly different from the pure oxide.

The analysis of the crystals showed that the average composition varied with the preparative conditions and generally preparations from the metal gave higher levels of doping. Typically, the sample for which lattice parameters are quoted above contained 1.1 ± 0.1 at.% antimony. The only significant impurities were found to be iron (0.03%) and copper (0.02%). Optical microscopy revealed that the blue coloration of these crystals was rarely homogeneous. Some parts of crystal clusters were a very pale blue color while other parts were dark blue-black and almost opaque.

Electron microscopy showed the crystals to possess a variable microstructure. Many of the crystal flakes examined were "perfect" and seemed to be identical to those found in pure $SnO_2$. However, an appreciable number of fragments contained planar faults which were

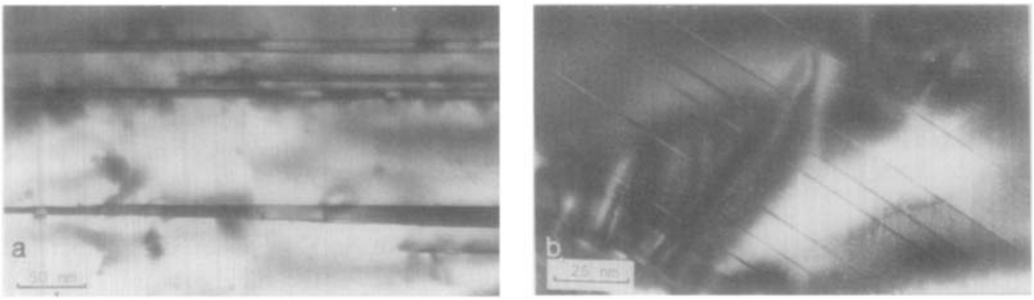

FIG. 2. (a) Crystal fragment containing narrow twins which show mostly as darker contrast in the lighter matrix. (b) Very narrow twin lamellae resembling isolated planar faults in the crystal fragment.

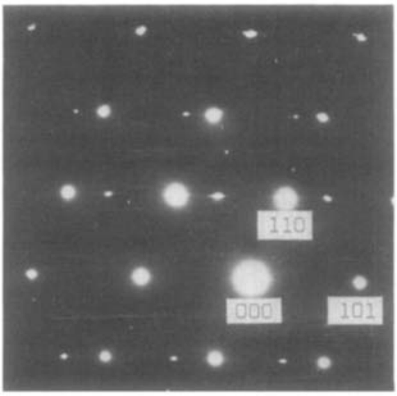

FIG. 3. Diffraction pattern from a twinned crystal of the type shown in Fig. 2a. The indices refer to the matrix reflections. The smaller spots are from the twins.

more often found in groups rather than completely isolated. Figure 2 shows typical examples of these boundaries. The contrast at these fault planes was consistent with $\alpha$-boundary contrast (*10*). Tilting of the crystals to bring the fault planes parallel to the electron beam allowed the planes to be indexed as $\{101\}$ type. Extra spots appeared on the electron diffraction patterns consistent with the faults being twin planes. When the faults were closely spaced as in Fig. 2b streaking was also observed on the diffraction pattern following the $\{101\}$ directions. Figure 3 shows an example of a typical diffraction pattern.

It was concluded that the boundaries were twin planes. The twins were sometimes wide, leading to essentially isolated twin planes, but more often the twin lamellae were narrow, similar to those shown in Fig. 2a. Occasionally the twin lamellae were very narrow being only about a nanometer in width, as shown in Fig. 2b. This type of repeated twinning is often found in mineral specimens of cassiterite which invariably contain high amounts of impurities (*16*) and was observed in crystals grown by both the chloride and chloride-free methods.

## Discussion

### *$SnO_2$ and CS Formation*

The present results show that $SnO_2$ forms relatively large crystals fairly easily and that they are virtually free of planar faults. The attempts at reduction yielded unchanged $SnO_2$ from a crystallographic point of view and showed that within the limits of our experiments $SnO_2$ has no appreciable stoichiometry range and does not form a series of *CS* phases analogous to its $TiO_2$ counterpart.

The reasons for this probably lie in the differences between the crystal chemistry of $Ti^{3+}$ and $Sn^{2+}$. In the case of $TiO_2$, the *CS* phases can be thought of as intergrowths of lamellae of the $Ti_2O_3$ (corundum) structure in the $TiO_2$ matrix, or alternatively as planes of collapse producing a sheet of ordered octahedrally coordinated interstitial $Ti^{3+}$ or $Ti^{4+}$ ions. Both $Ti^{3+}$ and $Ti^{4+}$ ions are of comparable size and both enjoy octahedral coordination.

In contrast to this the next lower tin ion to $Sn^{4+}$, $Sn^{2+}$, has a lone pair of electrons and does not readily enjoy octahedral coordination, as the discussion by Andersson and Åström (*11*) makes clear. From this point of view it is not surprising that *CS* phases do not form, because $Sn^{2+}$ will not readily enter the $SnO_2$ structures as interstitials in either octahedral (or tetrahedral) sites, and the SnO structure will not intergrow compatibly with the $SnO_2$ structure. Similar arguments suggest that $SnO_2$ will not have a large composition range due to random $Sn^{2+}$ ions, i.e., point defects, in the structure.

The differentiation between whether a material will tolerate point defects or prefer ordered or disordered planar faults is of some relevance here. Empirically a correlation exists that materials with very high static dielectric constants favor intergrowth, or the formation of *CS* phases, while materials with low dielectric constants favour point defects (*12*). From this point of view, therefore, it is of interest to note that the static dielectric constant of $SnO_2$ is about 12, compared to 100 to 200 for the rutile form of $TiO_2$. This suggests that if $SnO_2$ did possess any stoichiometry range, point defects, or point defect clusters would be favored. The theoretical aspects of this consideration are at present the subject of a study program, the results of which will be published in due course.

### *Antimony-Doped $SnO_2$*

As the atmosphere surrounding the crystals was not depleted in oxygen we suppose them to be fully oxidized. Although the phase diagram for the binary Sb–O system is not completely clear it is assumed that the equilibrium in the ternary Sn–Sn–O system is described by the $Sb_2O_4$–$SnO_2$ tie line and the doped crystals represent $SnO_2$–$Sb_2O_4$ phases at the preparation temperatures involved in our work.

The X-ray and analytical evidence shows that the crystals are very close in composition to $SnO_2$, but the strong blue color indicates that a significant change has taken place in the crystals compared with pure $SnO_2$. The most likely explanation of this blue coloration is that it is due to a charge transfer between $Sb^{3+}$ and $Sb^{5+}$ in the $SnO_2$ matrix rather than to the presence of $Sn^{2+}$. Similar dark blue coloration due to this charge transfer process has been observed by Atkinson and Day (*13*) in alkali metal–antimony halides of the $(NH_4)_2Sb_2Cl_6$ type, and related materials. In contrast, no blue-colored $Sn^{2+}$–$Sn^{4+}$ solid compounds have come to our attention, and Robin and Day do not list any in their extensive tabulation (*14*).

In order that charge transfer of this type should take place it is necessary for both the cations to be in similar geometrical sites and in close proximity to each other (*14*). The simplest way that this can be achieved is by the introduction of $Sb^{3+}$ and $Sb^{5+}$ ions into the $SnO_2$ matrix where they could occupy interstitial octahedral sites to form an oxide of composition $Sb_x^{3+}Sb_x^{5+}SnO_2$ or alternatively substitute into the tin positions to form an oxide of formula $(Sb_x^{3+}Sb_x^{5+})Sn_{1-2x}O_2$.

There are two drawbacks to this simple model. First, $Sb^{3+}$, like $Sn^{2+}$, possesses a lone pair of electrons and does not enjoy octahedral coordination (*16*). It is possible to argue that the charge transfer process, if rapid enough, would obscure this, as seems to occur in the ternary halides referred to above (*13*). Another problem is that the lattice parameter of antimony-doped $SnO_2$ does not differ significantly from that of pure $SnO_2$. In general both of the substitutions suggested above would tend to change the lattice parameter, but it is difficult to put a quantitative measure upon this, as although the octahedral radii of $Sb^{5+}$ (0.074 nm) and $Sn^{4+}$ (0.083 nm) are fairly precise (*15*) the radii of cations possessing lone pairs of electrons, such as $Sb^{3+}$ and $Sn^{2+}$ are uncertain and literature values are somewhat variable (*15*, *17*).

In terms of microstructure, the noticeable difference between doped and pure $SnO_2$ crystals was the presence of twins. Twinning is usually a form of stress relief in crystals, but it also provides a means of changing the anion to cation stoichiometry of a crystal slightly and of providing sites with different coordination to the normal crystal matrix. Since $Sb^{3+}$ ions do not enjoy octahedral coordination and the twin boundaries seem to be associated with the

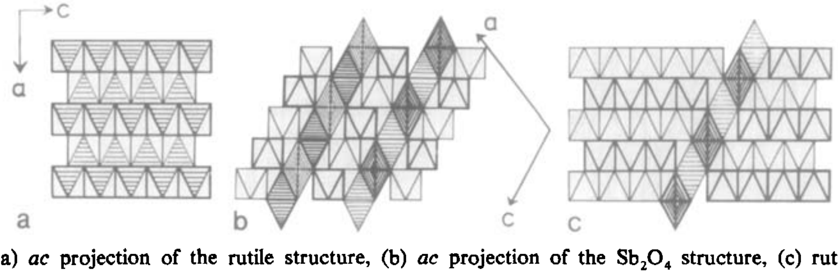

FIG. 4. (a) *ac* projection of the rutile structure, (b) *ac* projection of the $Sb_2O_4$ structure, (c) rutile structure containing one isolated lamella of Sb containing polyhedra, equivalent to an intergrowth between $Sb_2O_4$ and rutile. All structures are slightly indealized in these representations.

presence of antimony in the crystals, it is possible that this latter aspect of the twin boundaries is of importance here. If we suppose that antimony ions are segregated at the twin boundaries their influence upon the lattice parameter of the crystal would be negligible, and such segregation could put some or all of the $Sb^{3+}$ ions into more favorable sites from a crystal chemical viewpoint.

There are two ways in which this could take place. First, lamellae of the $Sb_2O_4$ structure can be intergrown coherently with the $SnO_2$ matrix to yield boundaries which would have similar diffraction contrast to normal twin boundaries in $SnO_2$ as shown in Fig. 4 (*11*). The $Sb^{3+}$ ions could be accommodated successfully in these regions. Alternatively, twin boundaries in rutile can generate a series of trigonal bipyramidal sites in the structure, provided that the twin plane is an oxygen plane in the crystal, as shown in Fig. 5. This type of coordination is reasonably acceptable to $Sb^{3+}$ ions and we can suppose that $Sb^{3+}$ ions could be favorably located in this region. These are, of course, not the only possible models, and the existence of the charge-transfer spectrum still requires a small amount of $Sb^{3+}$ to occupy octahedral sites. This, however, may occur in the neighborhood of the twin planes if the Sb concentration is highest in these regions.

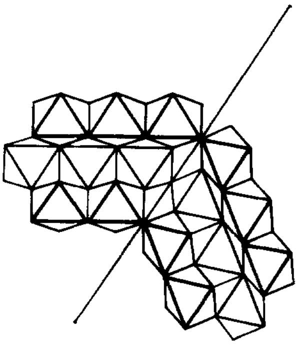

FIG. 5. *ac* projection of the rutile structure, slightly idealized, showing a possible (101)-type twin boundary.

At the present time, definite proof of whether antimony exists in or near these planar faults or whether it occurs in bulk $SnO_2$ as point defects or point defect clusters, has yet to be obtained. However, if the antimony is situated in or near to the observed planar faults, one would expect this to exert a somewhat different influence upon the chemical reactivity and physical properties of the material, and in particular upon the electrical properties than if it were homogeneously distributed. Future experiments are planned to explore these possibilities and to clarify the sites occupied by the antimony and its valence states. Work is also planned to determine to what extent the structures of these crystals are of relevance to the low-temperature preparations of antimony-doped $SnO_2$ used in catalysis.

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## References

1. D. B. ROGERS, R. D. SHANNON, A. W. SLEIGHT, AND J. L. GILLSON, *Inorg. Chem.* **8**, 841 (1969).
2. L. A. BURSILL AND B. G. HYDE, *Prog. Solid State Chem.* **7**, 177 (1972).
3. L. A. BURSILL, *J. Solid State Chem.* **10**, 72 (1974).
4. L. A. BURSILL AND G. G. STONE, *Philos. Mag.* **32**, 1151 (1975).
5. M. NAGASAWA, S. SHIONOYA, AND S. MAKISHIMA, *Jap. J. Appl. Phys.* **4**, 195 (1965).
6. D. F. MORGAN AND D. A. WRIGHT, *Brit. J. Appl. Phys.* **17**, 337 (1965).
7. P.-E. WERNER, *Ark. Kemi* **31**, 513 (1969).
8. J. A. MARLEY AND T. C. MACAVOY, *J. Appl. Phys.* **32**, 2504 (1961).
9. W. H. BAUR AND A. A. KHAN, *Acta Crystallogr. B* **27**, 2133 (1971).
10. S. AMELINCKX, *Surface Sci.* **31**, 296 (1972).
11. S. ANDERSSON AND A. ÅSTRÖM, *in* "Solid State Chemistry" (R. S. Roth and J. S. Schneider, Eds.),

N.B.S. Spec. Pub. 364, p. 3, Nat. Bur. Standards, Washington (1972).

*12.* R. J. D. TILLEY, *Nature* **269**, 229 (1977).

*13.* L. ATKINSON AND P. DAY, *J. Chem. Soc. A*, 2423 (1969).

*14.* M. B. ROBIN AND P. DAY, *Adv. Inorg. Radio Chem.* **10**, 247 (1967).

*15.* R. D. SHANNON, *Acta Crystallogr. A* **32**, 751 (1976).

*16.* W. A. DEER, R. A. HOWIE, AND J. ZUSSMAN, "Rock Forming Minerals," Vol. 5, p. 3. et seq., Longmans, London (1962).

*17.* J. GALY, G. MEUNIER, S. ANDERSSON, AND A. ÅSTRÖM, *J. Solid State Chem.* **13**, 142 (1975).