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Bursill L A & Hyde B G. Crystallographic shear in the higher titanium oxides: structure, texture, mechanisms and thermodynamics. *Prog. Solid State Chem.* 7:177-253, 1972.
[School of Chemistry, University of Western Australia, Nedlands, Australia]

Electron microscopic as well as thermogravimetric measurements of the higher titanium oxides were reviewed. Principles of crystallographic shear structures emerged clearly, establishing the concept of intergrowth in oxide crystal chemistry. [The *SCI*® indicates that this paper has been cited in over 145 publications.]

Intergrowth Phenomena in the Higher Titanium Oxides

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This work was the culmination of a five-year study of the higher titanium oxides by the authors. The latter range from Ti_2O_3 to TiO_2 including numerous ($\geq$50) ordered crystal structures Ti_nO_{2n-p} (n, p integers). The structural principles were established using the then-new techniques of high-resolution transmission electron microscopy. This chemical system is probably still the most thoroughly studied complex system involving homologous series (or families) of crystal structures related using Wadsley's intergrowth principle. Thus, two structural elements, in this case strings of the Ti_2O_3 (corundum-type) structure and sheets of TiO_2 (rutile), grow together coherently in integral ratios. Both the spacings and orientations of the intergrowths were shown to vary with stoichiometry of the components and temperature of preparation. The review also describes the results of a most painstaking thermogravimetric study of the oxidation and reduction kinetics in the range Ti_2O_3-TiO_2.

The longevity of the work is due to its unique combination of (1) direct structural information via electron microscopy, (2) thorough understanding of the crystallography of complex oxides, and (3) an in-depth thermodynamic study of the energetics and kinetics of the numerous oxide phases involved.

Our close study of the titanium oxides was fortuitous because it exhibited in reality the full range of intergrowth phenomena, which have been only mirrored to a lesser degree by numerous other solid-state systems. Researchers in the field of ceramic superconductors would dearly like to have similar chemical control over the system $Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+2}$ where it is desirable to obtain members having $n \geq 3$, in order to push the superconducting transition upwards from 125 K towards room temperature.[1]

1. Torardi C C, Subramanian M A, Calabrese J C, Gopalakrishnan J, Morrissey K J, Askew T R, Flippen R B, Chowdhry U & Sleight A W. Crystal structure of $Tl_2Ba_2Ca_2Cu_3O_{10}$, a 125 K superconductor. *Science* 240:631-4, 1988.