

GRAIN BOUNDARY SEGREGATION IN TITANIUM DIOXIDE

Q. Wang, G. Lian and E. C. Dickey

Department of Materials Science and Engineering, Pennsylvania State University, University Park, PA 16802

Solute segregation at grain boundaries in ceramics has significant ramifications for a variety of properties such as creep, grain growth and dielectric response. Semiconducting TiO₂ has been studied as a model system^{2,3} due to its well-known defect chemistry and relatively simple crystal structure. In our work, we have studied the local defect chemistry of TiO₂ doped with donor, acceptor and isovalent ions. The dopants were chosen such that we could explore the relative contributions of the elastic and electrostatic driving forces for segregation.

High purity (99.999%) rutile TiO₂ powder was selectively doped with Y, Ce or Nb, at concentrations ranging from 0.025 to 0.3 mole percent. The powders were isostatically pressed under 30,000 psi and sintering at 1300°C for about 5-10 hours in air. Thinned sections from the pellets were examined in a JEOL JEM 2010F field-emission transmission electron microscope operated at 200 kV and equipped with an annular dark field detector, scanning unit, Gatan GIF200 post column image filter and Oxford energy dispersive x-ray (EDX) detector.

High resolution TEM images (not shown) of the samples show no evidence for amorphous phases at grain boundaries in any of the samples. For 0.1 mol% doped samples, solute segregation was detected in the Y and Ce doped samples, but not in the Nb doped. Not until 0.3 mol% was Nb found to segregate to the grain boundaries. Fig. 1 shows a Z-contrast image of a 0.1 mol% Y-doped sample in which Y segregation is evidenced by the increased intensity of the grain boundary. From the Z-contrast images and complementary EDS profiles (Fig. 2) the level and distribution of solute segregation is quantified. Another important aspect of the grain boundary defect chemistry is the compensating defects for the Y substitution, which may be in the form of oxygen vacancies or titanium interstitials. Furthermore, identification of trap states such as Ti⁴⁺ → Ti³⁺ are necessary for understanding the local electronic structure. EELS spectra of Ti L_{2,3} and O K edges were used to quantify the Ti to O ratio and the Ti valence in the bulk and grain boundary. Figure 3, shows that no change in Ti:O ratio was observed between the grain interior and boundary area. Furthermore, as shown in Fig. 4, neither the chemical shifts or fine structure changes associated with Ti²⁺ or Ti³⁺ are evidenced at the boundary. Similar studies have been performed on the Ce and Nb doped samples. These experimental results will be discussed in relation to the theoretically predicted equilibrium defect chemistry.

Reference

1. J. A. S. Ikeda et al., *J. Am. Ceram. Soc.*, 76 (1993) 2437.
2. Y. -M. Chiang et al., *J. Am. Ceram. Soc.*, 41 (1994) 3.
3. M. F. Yan et al., *J. Appl. Phys.* 54 (1983) 764.

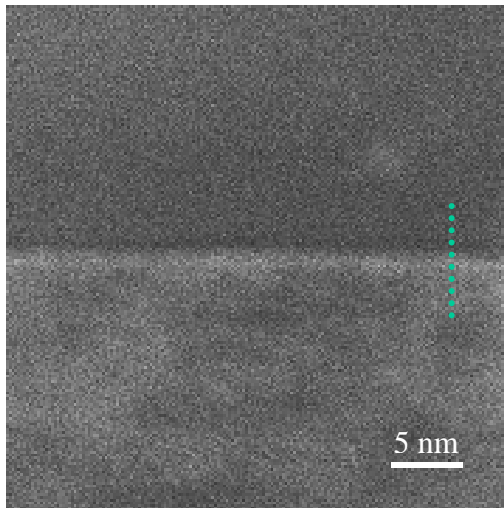


Figure 1. Z-Contrast STEM image shows Excess Y at the TiO_2 grain boundary.

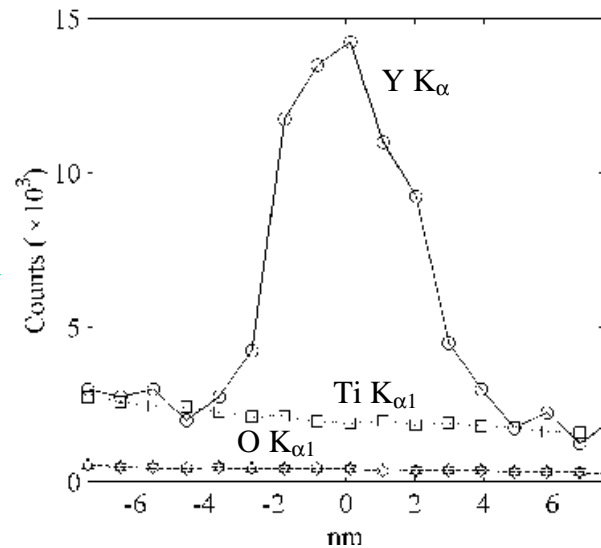


Figure 2. The interfacial excess of solute is quantified by EDS. The profile above reveals the spatial distribution of solute at the boundary.

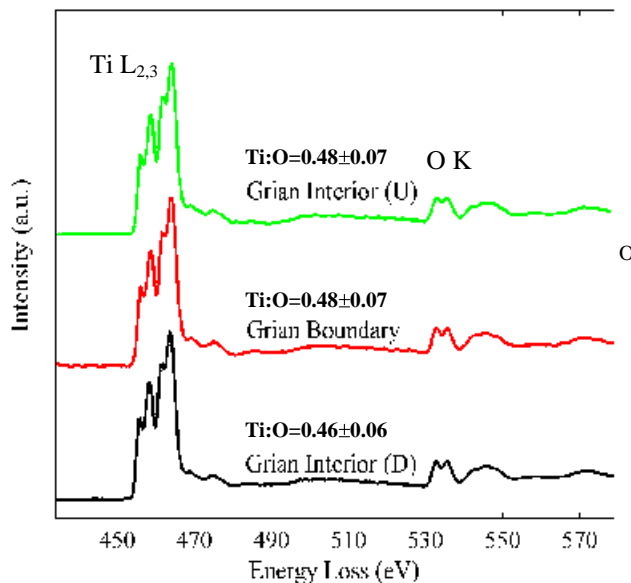


Figure 3. EELS spectra from the grain interior and grain boundary show that the Ti:O is unchanged at the boundary.

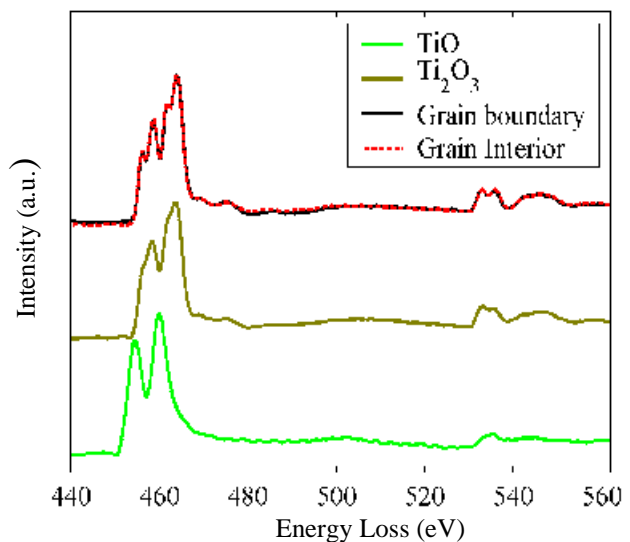


Figure 4. The oxidation state of the Ti ions is unchanged at the boundary as measured from the Ti $L_{2,3}$ edge. Reference spectra from TiO and Ti_2O_3 are shown for comparison.