Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Redox-Mediated Transformation of a Tb_2O_3(111) Thin Film from the Cubic Fluorite to Bixbyite Structure

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S1. O_2 TPD data obtained after the CF to bixbyite transformation

Figure S1 compares O_2 TPD spectra obtained after 9, 10 and 19 oxidation and reductions steps, with oxidation achieved by exposing the film to ~60 ML of O-atoms at 300 K. Figure S1 also shows an O_2 TPD spectrum obtained after the 20th oxidation step performed at 300 K and using an O-atom exposure of ~120 ML. This comparison reveals that the O_2 TPD traces after steps 9, 10 and 19 differ only slightly, and that doubling the O-atom exposure at the 20th step causes only a small increase (< 0.1 ML) in the O_2 TPD yield in the α-feature. The data thus supports the conclusion that the CF to bixbyite transformation effectively reaches completion after the 10th oxidation and reduction step.

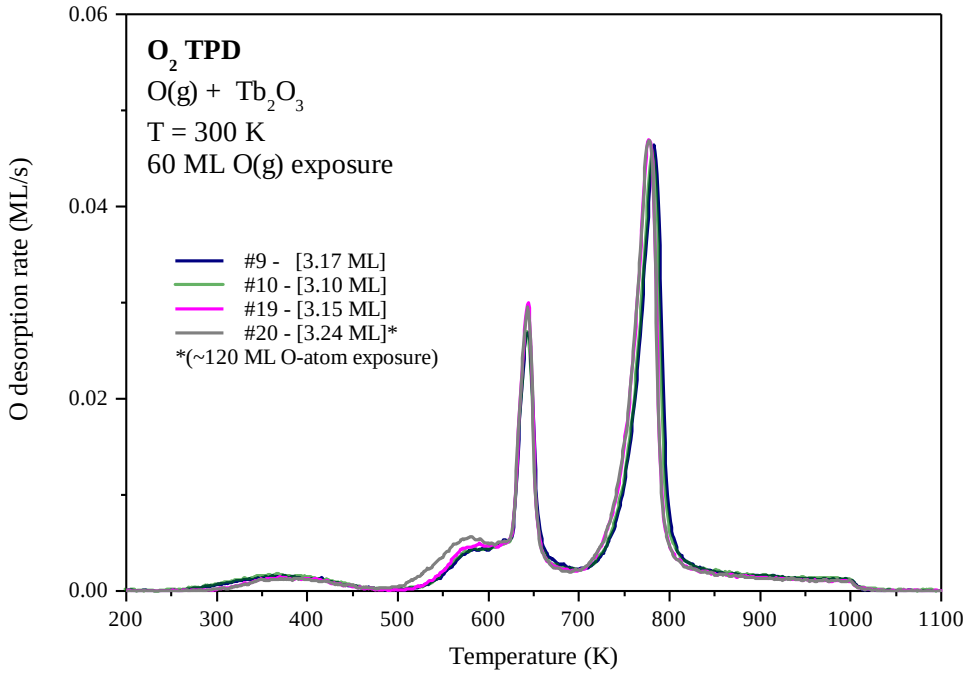

Figure S1: O_2 TPD spectra obtained after 9, 10 and 19 oxidation and reduction steps, with the O-atom exposure equal ~60 ML during the oxidation step. An O-atom exposure of ~120 ML was used in the 20th oxidation step.

S2. Estimates of oxide-phase quantities from O_2 TPD fits

We estimated the quantity of oxygen desorbing from the oxidized CF-TbO_x, δ-$Tb_{11}O_{20}$ and ι-Tb_7O_{12} phases by fitting the measured O_2 TPD spectra with peaks representing decomposition from each of these phases. Our goal was to obtain reasonable estimates of the O_2 TPD yields for the individual TPD peaks rather than to quantitatively reproduce the TPD peak shapes. For this purpose, we found it convenient to fit the ι and δ TPD peaks using Lorentz functions and the CF TPD peak using a Voigt function. Figure S2a shows measured and fit TPD peaks obtained from a reference ι-phase that we prepared by extensively oxidizing the final c-Tb_2O_3 film, and then heating to 700 K to desorb oxygen from the α and δ phases. We fit the resulting TPD spectrum using a single Lorentz function and obtain excellent agreement with the measured O_2 TPD yield.

We subsequently fit the O_2 TPD spectrum obtained from the oxidized CF-TbO_x film prior to heating to 1000 K to initiate the CF to bixbyite transformation. In this case, we fit the main, broad TPD feature arising from CF-TbO_x decomposition using a Voigt function and fit the small ι-peak (Figure S2b) by adjusting only the intensity of the Lorentz function for the ι-peak while keeping other peak parameters (center, width, etc) fixed at the values determined for the iota reference spectrum (Figure S2a). Similarly, we optimized a Lorentz function to fit the δ-peak observed in a TPD spectrum obtained after extensively oxidizing the final c-Tb_2O_3 film, and subsequently heating to 600 K to desorb oxygen from the α feature and thereby generating a TPD spectrum exhibiting only the δ and ι peaks (not shown).

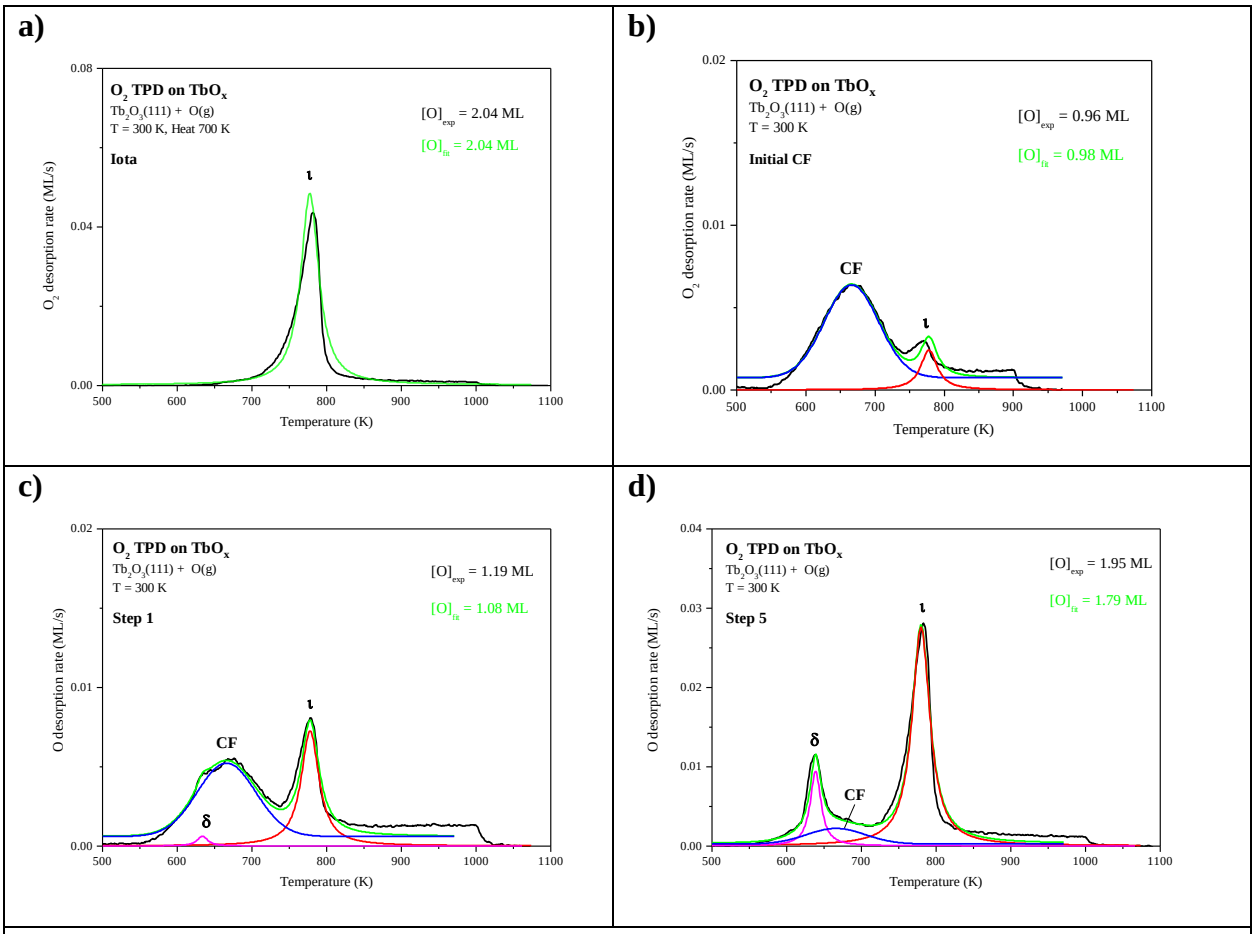

Figure S2: a) Measured and Lorentz fit of an O_2 TPD spectrum for the reference ι-phase, b) Measured and total fit of an O_2 TPD spectrum obtained after oxidizing the initial CF-Tb_2O_3 film. The measured spectrum was fit using the Lorentz peak determined in a) and a Voigt function to fit the broad CF peak. Measured and fitting peaks for c) Redox Step 1 and d) Redox Step 5.

After setting the individual peak parameters as described above, we fit O_2 TPD spectra for each redox step by optimizing the intensities of the CF, δ and ι peaks. Figures S2c and d compare measured O_2 TPD spectra for Steps 1 and 5 with the individual fit peaks and their sum, i.e., the total fit spectrum. We find that the fit spectra reproduce the measured O_2 TPD yields to within better than about 10%.