Supporting Information

Redox-Mediated Transformation of a Tb$_2$O$_3$(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 20$^{th}$ 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 20$^{th}$ step causes only a small increase ($<$ 0.1 ML) in the O$_2$ TPD yield in the $\alpha$-feature. The data thus supports the conclusion that the CF to bixbyite transformation effectively reaches completion after the 10$^{th}$ oxidation and reduction step.
Figure S1: \( \text{O}_2 \) TPD spectra obtained after 9, 10 and 19 oxidation and reduction steps, with the O-atom exposure equal \( \sim 60 \) ML during the oxidation step. An O-atom exposure of \( \sim 120 \) ML was used in the 20th oxidation step.

### S2. Estimates of oxide-phase quantities from \( \text{O}_2 \) TPD fits

We estimated the quantity of oxygen desorbing from the oxidized CF-TbO\(_x\), \( \delta \)-Tb\(_{11}\)O\(_{20}\) and \( \tau \)-Tb\(_7\)O\(_{12}\) phases by fitting the measured \( \text{O}_2 \) TPD spectra with peaks representing decomposition from each of these phases. Our goal was to obtain reasonable estimates of the \( \text{O}_2 \) 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 \( \tau \) and \( \delta \) 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 \( \tau \)-phase that we prepared by extensively oxidizing the final c-Tb\(_2\)O\(_3\) film, and then heating to 700 K to desorb oxygen from the \( \alpha \) and \( \delta \) phases. We fit the resulting TPD spectrum using a single Lorentz function and obtain excellent agreement with the measured \( \text{O}_2 \) 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 $\iota$-peak (Figure S2b) by adjusting only the intensity of the Lorentz function for the $\iota$-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 $\delta$-peak observed in a TPD spectrum obtained after extensively oxidizing the final c-Tb$_2$O$_3$ film, and subsequently heating to 600 K to desorb oxygen from the $\alpha$ feature and thereby generating a TPD spectrum exhibiting only the $\delta$ and $\iota$ peaks (not shown).
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 τ 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%. 

Figure S2: a) Measured and Lorentz fit of an O$_2$ TPD spectrum for the reference τ-phase, b) Measured and total fit of an O$_2$ TPD spectrum obtained after oxidizing the initial CF-Tb$_2$O$_3$ 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.