Supplemental Information
Combinatorial substrate epitaxy: a new approach to growth of complex metastable compounds†

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1 Supplemental Results and Discussion

In Fig. S 1(a-c) and Fig. S 2(a-c), example EBSD patterns are given from $Sr_2Nb_2O_7$ substrate grains. They are intense and have sharp contrast, similar to those given in Fig. 2(a-c) and Fig. 3(a-c). Within any individual grain, the patterns and orientation assignments were consistent. The EBSD patterns were indexed by the TSL software to determine a surface plane orientation, were expressed as Miller indices, and are given in Fig. S 1(a-c) and S 2(a-c). The surface planes are within 5 ° of the indices listed. As expected, a wide orientation spread is available on the sintered pellets- ranging in just these six grains from (001) to (552) (and from (110) to (315) in the grains given in Fig. 2 and Fig. 3).

Kikuchi patterns registered after deposition of ≈ 70 nm of $La_2Ti_2O_7$ and $Gd_2Ti_2O_7$ are given respectively in Fig. S 1(d-f) and Fig. S 2(d-f), for the same grains whose patterns are given respectively in Fig. S1(a-c) and S2(a-c). In all cases, film patterns have less distinct contrast for both compositions and all orientations, but they are similar to the substrate patterns. It is important to remember that the Kikuchi patterns can be rotated owing to remounting, could be slightly different as the known materials in the titanate and niobate systems can have different (though related) crystal structures (monoclinic or orthorhombic), and could be rotated owing to misfit accommodation mechanisms.

The similarity of the Kikuchi patterns from the films (keeping in mind that the patterns come from the last ≈ 40 nm of the 70 nm film) and substrates indicate that the films grew epitaxially. The film orientations are given in Fig. S 1(d-f) and Fig. S 2(d-f); the films have identical orientations to the substrates for these six grain-orientations. In fact, we did not find any orientations on which an epitaxial phase did not grow: in other words, we did not find any orientations where the patterns were not identical to the underlying substrate grain. $La_2Ti_2O_7$ is stable in the 110-*LP* structure in the bulk, so this epitaxial growth in not surprising. The stable bulk polymorph of $RE_2Ti_2O_7$ for *RE* = Gd, Sm, and Dy compositions is py-

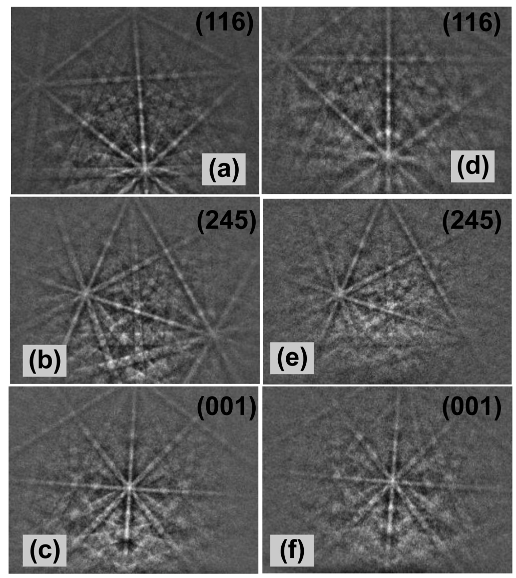

Fig. S 1 Electron backscatter diffraction patterns from the $Sr_2Nb_2O_7$ substrate (a-c) and the $La_2Ti_2O_7$ film (d-f). In each case, the surface plane determined from the measured Euler angles is given, and these are identical (within the uncertainty) for each grain before and after film deposition. Substrate (film) Euler angles (°) are: Grain a (d)– 7 (3), 83 (85), 21 (8); Grain b (e)– 4 (12), 49 (53), 21 (29); Grain c (f)– 173 (181), 94 (82), 141 (136).

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rochlore. These results support the assertion that the polycrystalline surfaces promote complex epitaxy of metastable phases and that EBSD is an effective local probe for structural characterization.

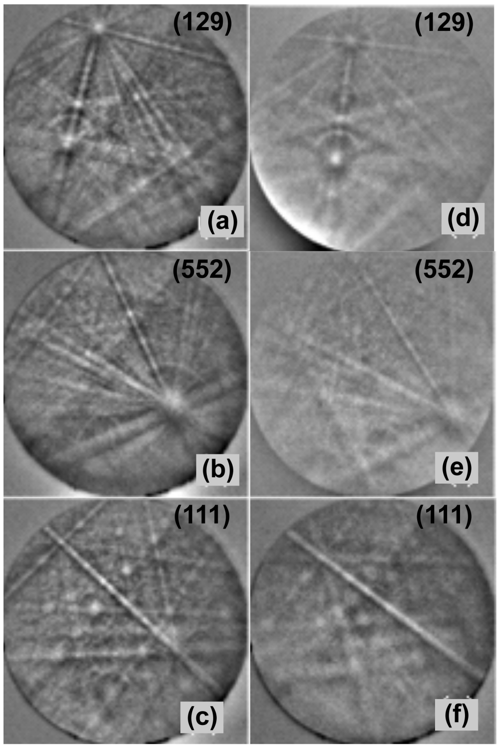

Fig. S 2 Electron backscatter diffraction patterns from the $Sr_2Nb_2O_7$ substrate (a-c) and the $Gd_2Ti_2O_7$ film (d-f). In each case, the surface plane determined from the measured Euler angles is given, and these are identical (within the uncertainty) for each grain before and after film deposition. Substrate (film) Euler angles (°) are: Grain a (d)– 165 (173), 90 (82), 299 (295); Grain b (e)– 249 (277), 30 (27), 134 (105); Grain c (f)– 314 (338), 78 (87), 322 (301).

A HREM image of the interface between an epitaxially stabilized $Sm_2Ti_2O_7$ film and the $Sr_2Nb_2O_7$ substrate is shown in Fig. S 3. The inset shows the FFT of the substrate region, which can be indexed as the $(011)_o$ zone axis. The contrast in the film and substrate is quite good; the interface (marked with short white lines and bracketed by long black lines to guide the eye) is reasonably sharp at the atomic scale. There is a correspondence in the contrast (atomic planes) of the HREM between the substrate and the film, clearly indicating the high quality epitaxy between the complex structures on the polycrystalline ceramic substrates. Based on this indexation, the two white, nearly-vertical lines crossing the film-substrate interface drawn on the sides of the image are parallel to $(0\bar{1}1)_o$ planes. Between the two white lines, there are 93 (97) parallel planes of contrast in the substrate (film); the regions of distorted contrast at the interface correspond to the locations of misfit dislocations that accommodate this difference. This result corroborates that the films are relaxed (the number of extra planes agrees reasonably with the lattice parameter decrease expected for a titanate).

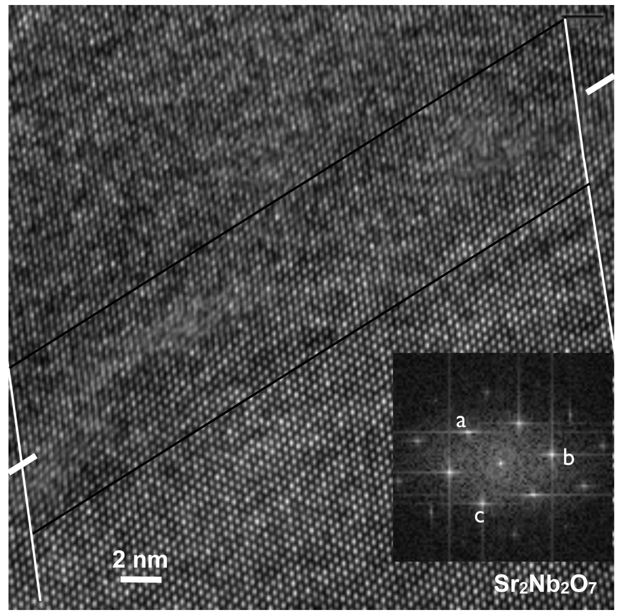

Fig. S 3 HREM image from a cross section of the grain marked 3 in Figure 1(b). Black lines are guides bracketing the wavy interface marked by short white lines. Long white lines are guides connecting similar contrast across the interface, which are consistent with the $(0\bar{1}1)$ planes. The inset gives the FFT of the image, which corresponds to a 011 zone axis diffraction pattern, where the spots a, b, and c correspond respectively to $(\bar{1}1\bar{1})$, $(11\bar{1})$, and $(0\bar{2}2)$.