Supplementary information for 'A Solution Chemistry Approach to Epitaxial Growth and Stabilisation of $Bi_2Ti_2O_7$ Films'.

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Experimental details

Samples were prepared by a spin coating technique. Bismuth nitrate pentahydrate (Aldrich, ≥99.99%) and titanium(IV) isopropoxide (Aldrich, 99.999%) were dissolved in acetic acid (Fischer Scientific, analytical grade) in a 1:1 mol ratio to give 5 cm^3 of a solution with 1 M total metal concentration, which was diluted with 2.5 cm^3 2-metoxy-ethanol. The resulting solution was used to spin coat (001), (110) and (111)-oriented YSZ substrates at 3000rpm. Previous coating, the substrates were cleaned by rinsing in ethanol. After coating, substrates were dried in a convection oven at 200°C. This led to amorphous films that were calcined for 5 h at temperatures ranging from 600°C up to 900°C to form epitaxial films of pyrochlore $Bi_2Ti_2O_7$. One coat-drying cycle was enough to produce continuous films, whose thickness can be controlled by increasing the number of cycles. However the study presented in this report was done using one-cycle thin films.

Following alignment of the crystal specular θ-2θ X-ray diffractograms were measured using a PANalytical X'Pert Pro diffractometer incorporating a Cu Kα source. Following the θ-2θ scans, Φ scans were carried out for each sample in the [113] direction.

Low energy ion scattering (LEIS) spectra were measured in a Qtac 100 instrument (ION-TOF GmbH) fitted with a double toroidal energy analyser (DTA). The samples were analysed using a He^+ primary ion beam directed perpendicularly to the target surface in a 1 μm^2 spot size with 3 keV energy and analyser pass energy of 3 keV. The cleaning process was completed by an *in-situ* atomic-oxygen treatment, which was done until the last spectrum was the same (within error) to the previous one. Atomic-oxygen treatment periods were approximate 1 hour for the first treatment and 30 min for the following ones. Typically the cleaning process was composed of two atomic-oxygen treatments. Low-energy sputtering was performed by 1 keV Ar^+ bombardment at an angle of 59°. The sputtered area was 2 μm^2 and it was ensured that the analysis spot size sits well within this area.

X-ray photoelectron spectra (XPS) were taken with Thermo Scientific K-Alpha spectrometer using a 72 W monochromated Al K alpha source (*hv* = 1486.6 eV). The X-rays are microfocused at the source to give a spot size on the sample of 400 microns in diameter. The analyser is a double focusing 180 degree hemisphere with mean radius 125 mm. It is run in constant analyser energy (CAE) mode. The pass energy was set to 200 eV for survey scans and 50 eV for high resolution regions. All XPS were referenced according to the adventitious C 1s peak (285 eV).

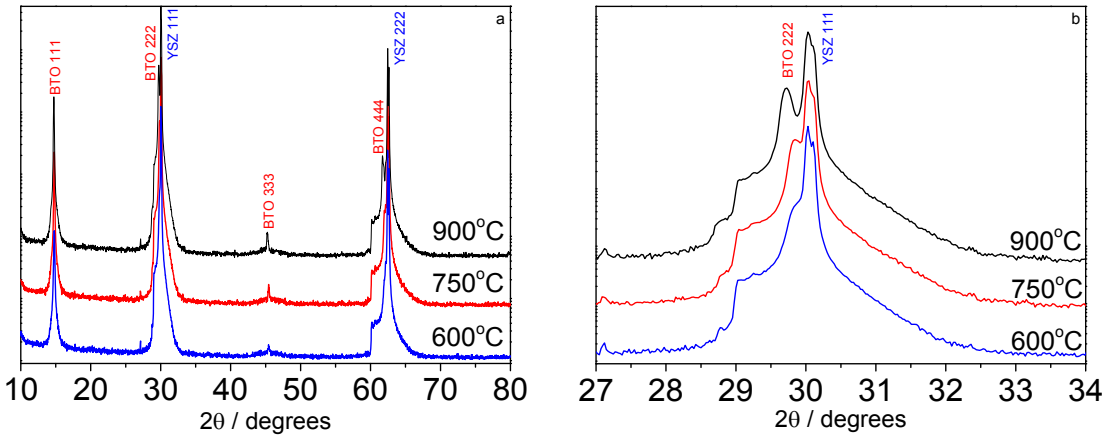

Figure S1. (a) X-ray diffractograms of $Bi_2Ti_2O_7$ films deposited on (111)-oriented YSZ after annealing at 600°C, 750°C and 900°C. (b) Expanded X-ray diffractograms in the $Bi_2Ti_2O_7$ (222) / YSZ (111) region. $Bi_2Ti_2O_7$ films crystallise at temperatures as low as 600°C. It can be seen that annealing the originally amorphous $Bi_2Ti_2O_7$ film in the 600°C to 900°C temperature range leads to the growth of single crystalline films epitaxial to the YSZ substrate with no secondary phase segregation.

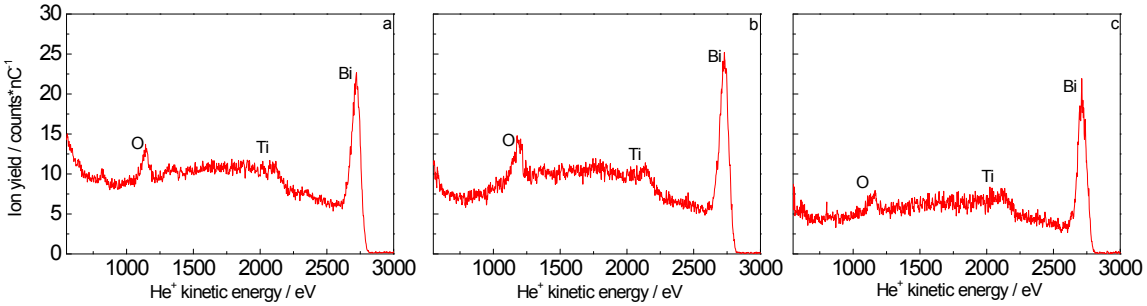

Figure S2. LEIS spectra of (a) (111)-, (b) (110)- and (c) (001)-oriented $Bi_2Ti_2O_7$ single crystal calcined at 750°C. Characteristic peaks for bismuth and oxygen can be seen in the He^+ scattering spectrum at 2700 eV and 1200 eV, respectively for the three crystalline surfaces studied in this work. Although no spectral peak can be detected in titanium region, 2125 eV, there is a clear background enhancement in this area in all spectra. This spectrum suggests that the surface of the single crystalline $Bi_2Ti_2O_7$ films terminates in a BiOx-like structure, but titanium atoms are present in atomic layers directly underneath this termination