Supplementary information

Strain evolution and in-situ phase transitions in freestanding $BaTiO_3$ epitaxial membranes *via* $La_{2/3}Sr_{1/3}MnO_3$ sacrificial layer

K Gurukrishna[a], Aditya Uday Kamat[a], Rishow Kumar[a], Ashish Garg[b], Shikhar Misra[a]*

[a] Department of Materials Science and Engineering, Indian Institute of Technology Kanpur, Kanpur, Kalyanpur 208016, UP, India

[b]Department of Sustainable Energy Engineering, Indian Institute of Technology Kanpur, Kalyanpur, 208016 UP, India

Synthesis of LSMO target

$La_{2/3}Sr_{1/3}MnO_3$ (LSMO) PLD target was synthesised *via* conventional solid-state reaction route. High-purity powders (4N) of La_2O_3, $SrCO_3$, and Mn_2O_3 were stoichiometrically weighed, and blending was done in an agate mortar for 2 hrs. Calcination of the blended powder was carried out at 1100 °C for 12 hrs using a tube furnace followed by natural air cooling. Calcined powder was then milled again and compacted using a uniaxial hydraulic press with a load of about 13 tons. The circular disc-shaped pellet of 1 inch diameter with 3 mm thickness was then sintered at 1300 °C for 12 hrs. The phase formation was confirmed using X-ray diffraction. The XRD profile of LSMO target is shown in Fig.S1

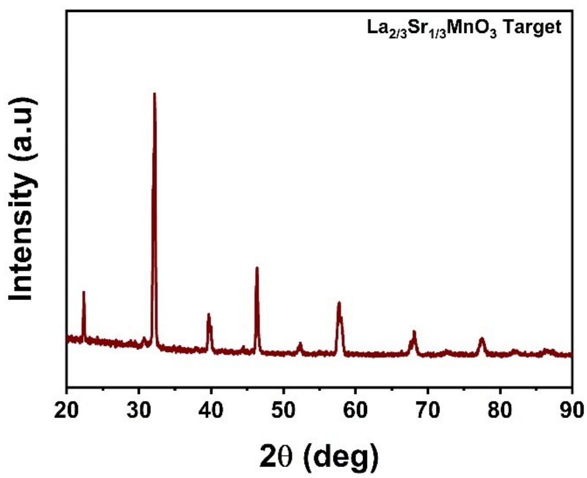

Figure S1: XRD profile of LSMO PLD target

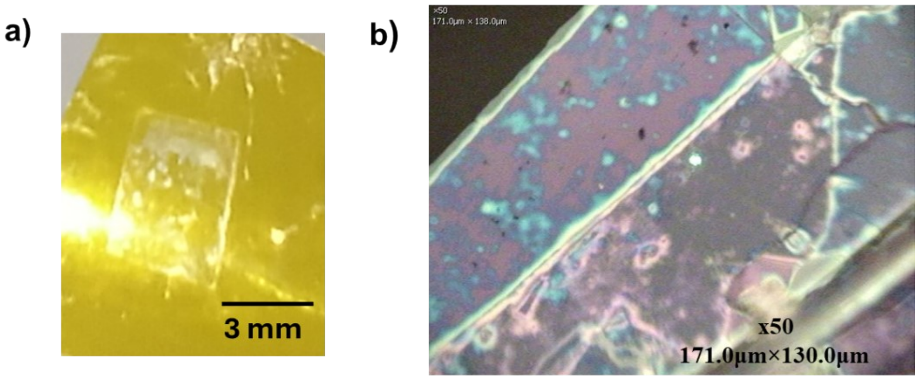

Figure S2: a) photograph of BTO membrane and b) Optical microscope image of BTO membrane on glass

The strained BTO layer exhibits a reduced c-axis value of 4.027 ± 0.001 Å (c = 4.033 Å for bulk $BaTiO_3$)[1], corresponding to a compressive strain of $\varepsilon_c = -0.15\%$. Supplementary Figure S3 reveals a lower-angle shift in the (002) XRD reflection for the membrane, indicating slight relaxation with a lattice constant of 4.029 ± 0.001 Å ($\varepsilon_c = -0.10\%$).[2]

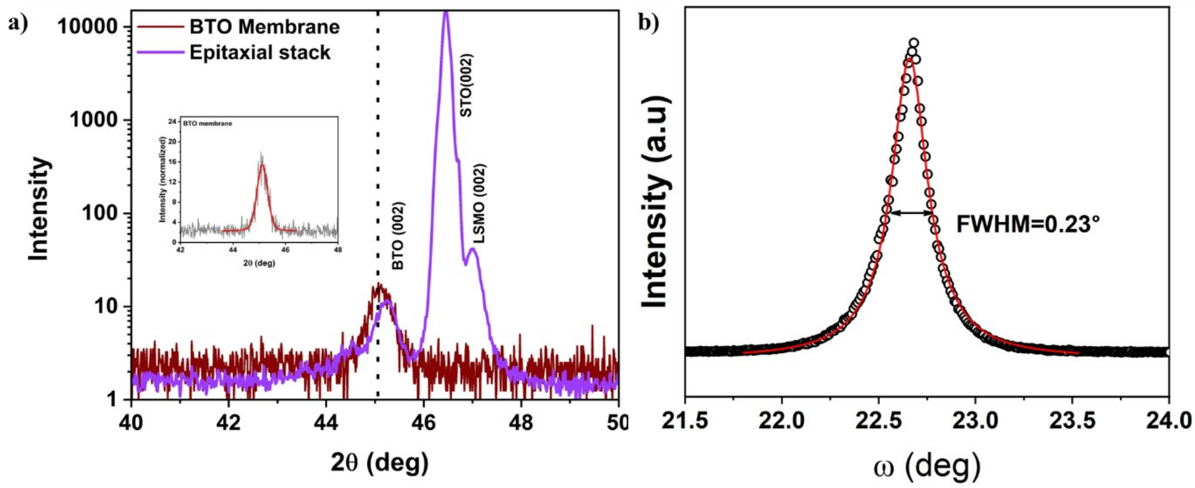

Figure S3: a) *θ-2θ* XRD profile of BTO membrane and the strained thin film stack with Y axis showing the normalized intensity; The inset showing the fit to pseudo-Voight function. b) rocking curve of the epitaxial BTO before etching.

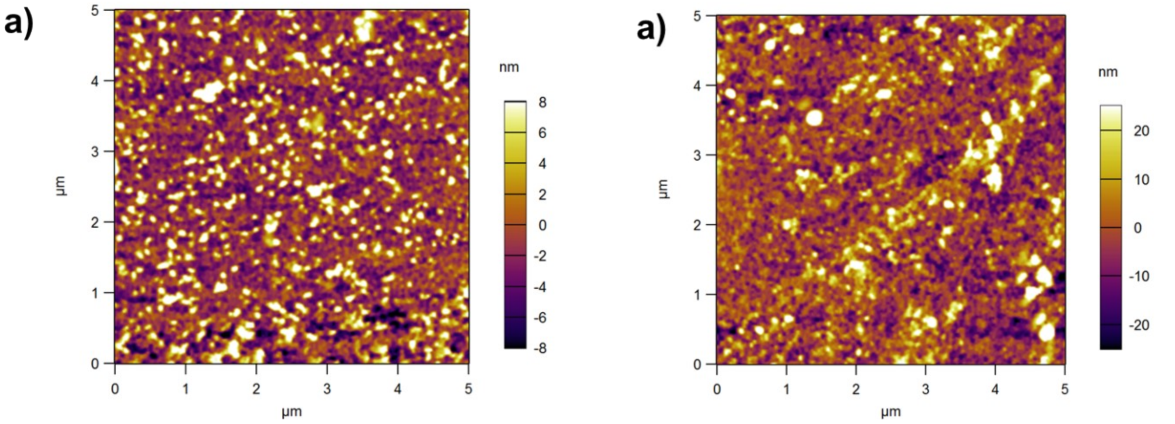

*Figure S*4: AFM micrographs of a) BTO epilayer and BTO membrane at identical aerial scans

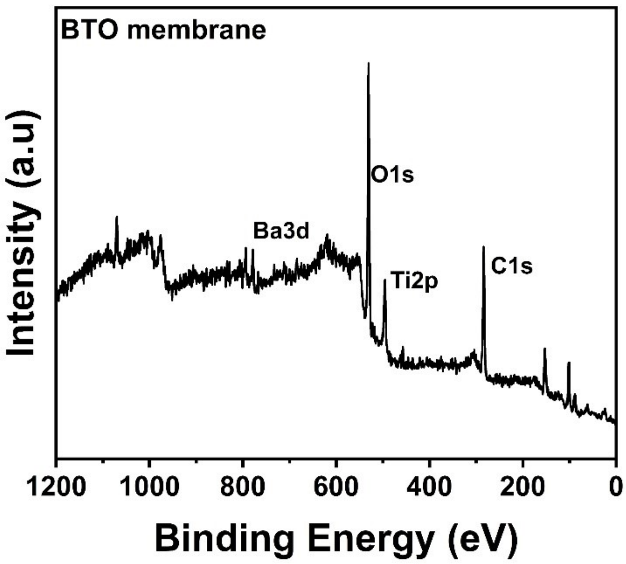

Figure S5: XPS Survey spectra of BTO membrane on glass substrate

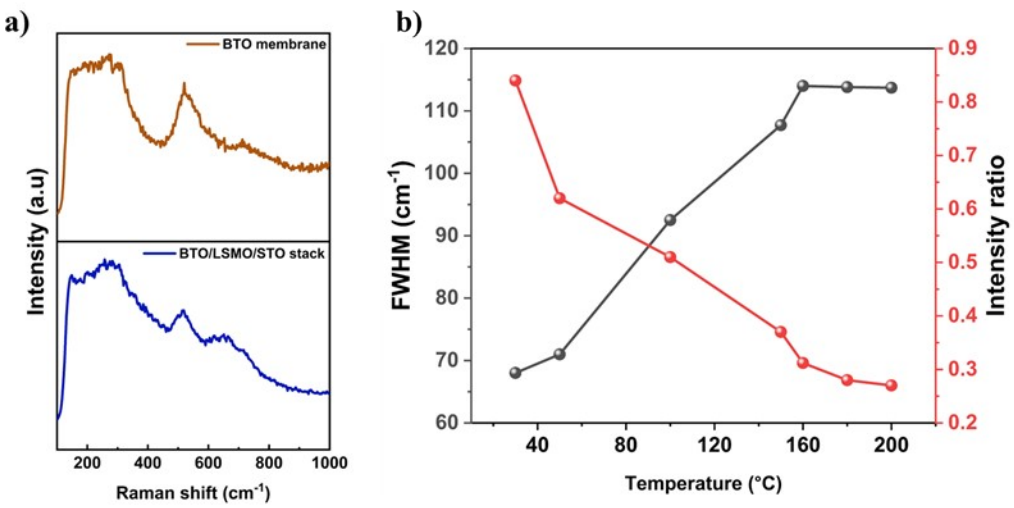

Figure S6: a) Ambient Raman spectra of BTO membrane and strained layer and b) depiction of variation in full width at half maxima (FWHM) and change in intensity ratio of the Raman mode at 521cm^{-1}

The ratio of the peak intensity was calculated as

$$I_{ratio} = \frac{I_{peak} - I_{baseline}}{I_{baseline}}$$

Where, I_{peak} and $I_{base\ line}$ are the intensities of the peak and the baseline.

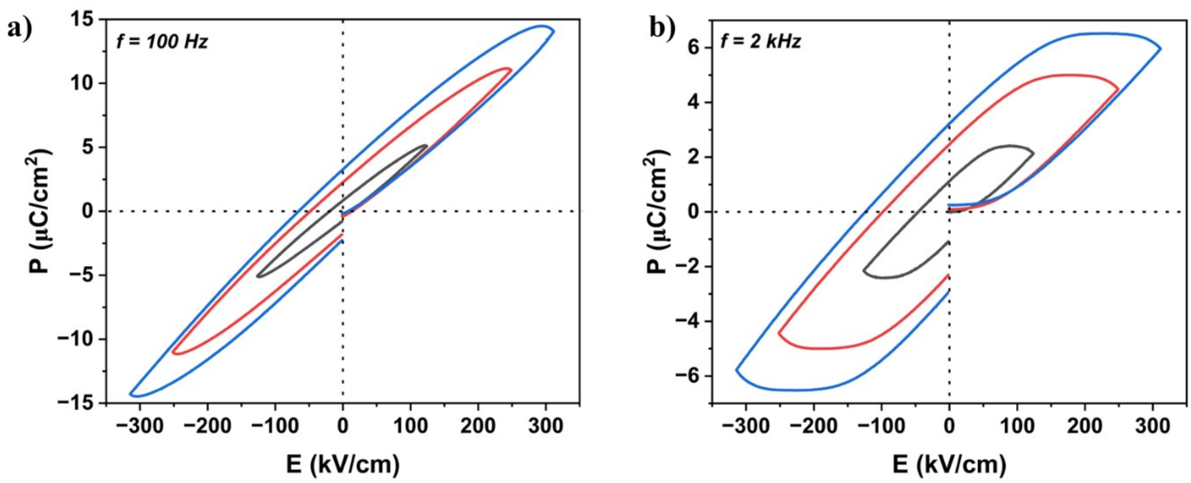

Figure S7: ferroelectric polarisation versus electric field loops (P-E) of strained BTO layer measured at a) 100 Hz and b) 2 kHz frequencies.

Existence of ferroelectric properties in the thin film stacks are assessed by polarisation – electric filed (P-E) loop characteristics as shown figure S7. The loops recorded at 2 kHz reveal a polarization value of 2Pr ≈ 6.4 μC/cm² and a coercive field Ec ≈ 93.8 kV/cm, indicating satisfactory ferroelectric behavior.

References

[1] Y.S. Kim, D.H. Kim, J.D. Kim, Y.J. Chang, T.W. Noh, J.H. Kong, K. Char, Y.D. Park, S.D. Bu, J.G. Yoon, J.S. Chung, Critical thickness of ultrathin ferroelectric $BaTiO_3$ films, Appl Phys Lett 86 (2005) 1–3. https://doi.org/10.1063/1.1880443.

[2] F. He, B.O. Wells, Lattice strain in epitaxial $BaTiO_3$ thin films, Appl Phys Lett 88 (2006). https://doi.org/10.1063/1.2194231.