

# Supplementary Materials: Tunability Investigation in the BaTiO<sub>3</sub>-CaTiO<sub>3</sub>-BaZrO<sub>3</sub> Phase Diagram Using a Refined Combinatorial Thin Film Approach

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## 1. BCTZ films structure and microstructure characterizations

An optimization of the deposition conditions in terms of substrate temperature, oxygen dynamic pressure and laser fluence, was done for each target separately prior to CPLD synthesis of the libraries. The polycrystalline IrO<sub>2</sub> electrode of this study was chosen to promote a polycrystalline growth of BCTZ, as it is found in commercial BST-based varactors. The resulting X-ray diffraction signal is weak making growth optimization difficult. We used instead SrTiO<sub>3</sub> single crystal substrates to optimize the growth using X-ray diffraction. Then a common set of deposition parameters leading to good film crystallinity and roughness for all the targets used in CPLD synthesis of the libraries was selected, i.e. a KrF excimer laser fluence of 2 J/cm<sup>2</sup>, a substrate temperature of 700 °C and a dynamic oxygen pressure of 0.3 mbar.

### 1.1. Ba<sub>0.785</sub>Ca<sub>0.215</sub>Ti<sub>0.715</sub>Zr<sub>0.285</sub>O<sub>3</sub> films on SrTiO<sub>3</sub> (001) substrate

A diffractogram of a Ba<sub>0.785</sub>Ca<sub>0.215</sub>Ti<sub>0.715</sub>Zr<sub>0.285</sub>O<sub>3</sub> film grown in these conditions is shown in Figure S1 (a). Only (001) peaks from the BCTZ films are seen, as expected for an epitaxial growth on SrTiO<sub>3</sub> (STO) (001) oriented substrate. There is no sign of any parasitic phase. Furthermore the fringes observed around (001) and (002) diffraction peaks (see blow-ups in Figure S1 (a)) indicate a very good crystalline quality of BCTZ/STO interface and of BCTZ surface. This was confirmed by atomic force microscopy (AFM) as can be seen in the surface topography image shown in Figure S1 (b). A rms roughness of 0.3 Å was extracted from this 10 × 10 μm<sup>2</sup> scan.

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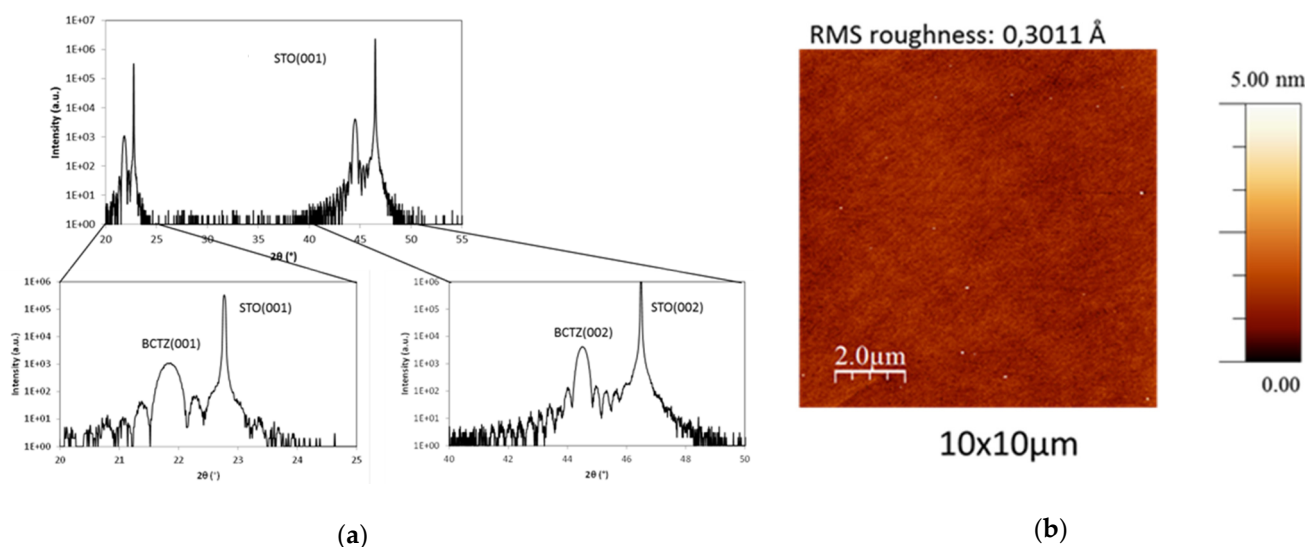
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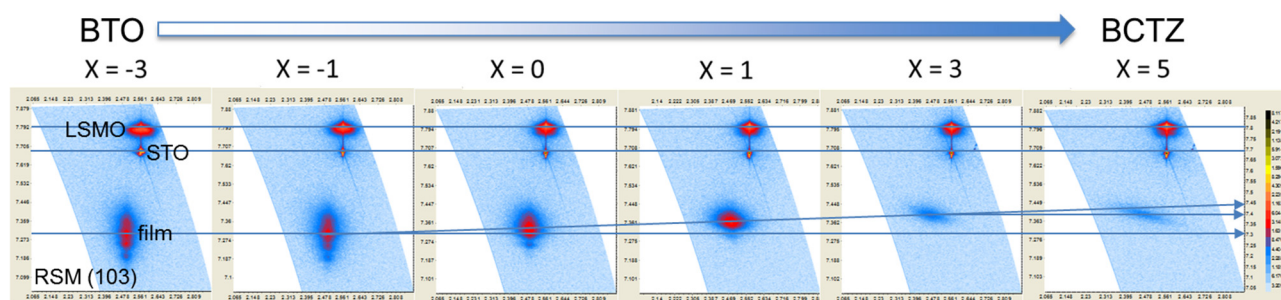
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**Figure S1.** (a) Diffractogram of a  $\text{Ba}_{0.785}\text{Ca}_{0.215}\text{Ti}_{0.715}\text{Zr}_{0.285}\text{O}_3$  film; (b) AFM surface topography image of the same  $\text{Ba}_{0.785}\text{Ca}_{0.215}\text{Ti}_{0.715}\text{Zr}_{0.285}\text{O}_3$  film.

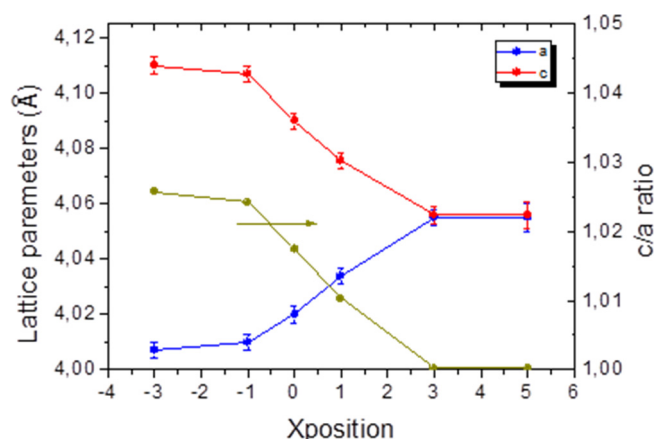
### 1.2. Epitaxial $\text{BaTiO}_3$ - $\text{Ba}_{0.785}\text{Ca}_{0.215}\text{Ti}_{0.715}\text{Zr}_{0.285}\text{O}_3$ library deposited on $(\text{La,Sr})\text{MnO}_3/\text{STO}$

Once a set of deposition conditions were fixed, polycrystalline CPLD libraries were grown on  $\text{IrO}_2/\text{Si}$ . Again in order to characterize the crystallinity of the libraries as well as to investigate the evolution of the lattice parameters, we deposited the same libraries on (001) STO with an oxide electrode of  $(\text{La,Sr})\text{MnO}_3$ . Reciprocal space maps (RSM) around the (103) STO node were measured along the gradient every mm. A 1 mm slit was used to reduce the x-ray beam footprint width on the sample along the gradient direction while maintaining a sufficiently high signal for RSM. An example of RSMs measured at various X position along the gradient of the  $\text{BaTiO}_3$ - $\text{Ba}_{0.785}\text{Ca}_{0.215}\text{Ti}_{0.715}\text{Zr}_{0.285}\text{O}_3$  library is shown in Figure 2.



**Figure S2.** RSMs around the (103) node measured at various X position along the gradient of the  $\text{BaTiO}_3$ - $\text{Ba}_{0.785}\text{Ca}_{0.215}\text{Ti}_{0.715}\text{Zr}_{0.285}\text{O}_3$  library grown on  $(\text{La,Sr})\text{MnO}_3/\text{STO}$ .

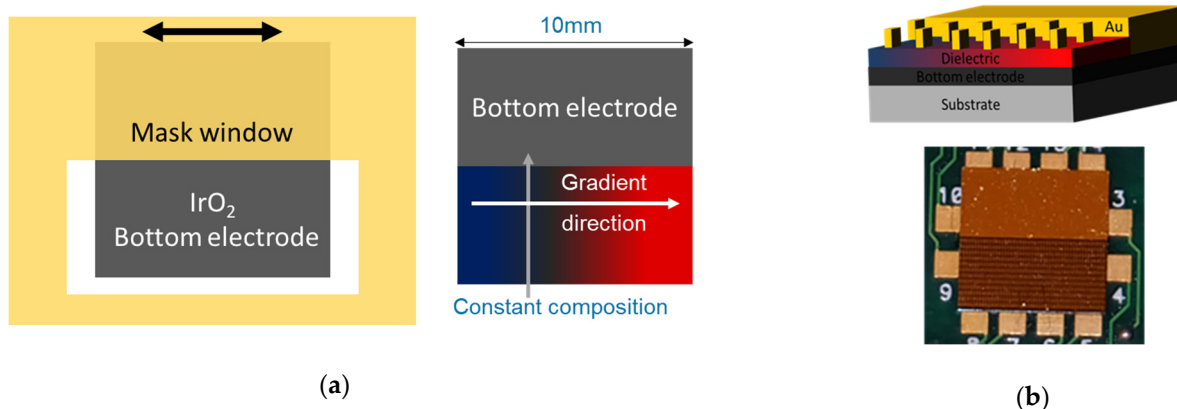
The BCTZ peaks in Figure S2 are vertically and horizontally offset from STO peaks. This is expected from an epitaxial growth of BCTZ followed by film relaxation after a critical thickness due to the large lattice parameter mismatch with STO. One can furthermore see the evolution of BCTZ peak position along the gradient direction. The corresponding BCTZ in-plane and out-of plane lattice parameters evolution is represented in Figure S3, together with the tetragonality, versus position.



**Figure S3.** BCTZ in-plane and out-of plane lattice parameters, and c/a tetragonality, versus position.

## 2. Fabrication of composition spread libraries

To localize on the substrate the deposition coming from each target we used a shadow mask with a rectangular aperture (see Figure S4 (a) left). Half of the IrO<sub>2</sub> bottom electrode (BE) remained covered at all time for future direct electrical access. A schematic of the obtained libraries in Figure S3 (a) right illustrates the direction of the gradient (horizontal) and lines of constant composition (vertical lines). After Au sputter deposition of top electrodes and BE contact pad, the library is ready for impedance spectroscopy characterization. A schematic of a finalized library is shown in Figure S4 (b) top, together with a top view picture of an actual library in Figure S4 (b) bottom. The contact pads geometry allows for automated probing on a Cascade probe station.



**Figure S4.** (a) Schematics of the shadow-mask deposition process and of the obtained CPLD libraries; (b) Schematic (top) and top view picture (bottom) of a finalized library.

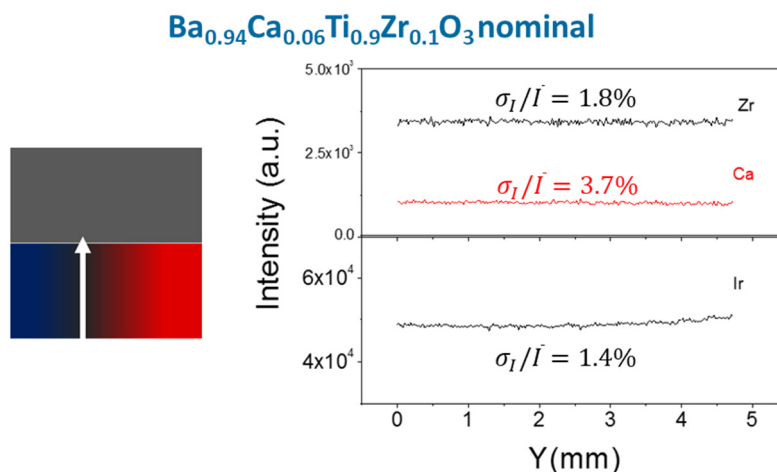
## 3. Electron Probe Micro Analysis

Ba and Ti peaks are overlapped with Energy Dispersive X-ray spectroscopy making this technique unsuitable for BCTZ elemental analysis. Electron Probe Micro Analysis with Wavelength Dispersive Spectroscopy (WDS) allows for Ba and Ti peaks separation and was used to qualitatively and quantitatively characterize BCTZ libraries.

### 3.1. Thickness and composition homogeneity at constant composition

The first thing to check in BCTZ libraries is that the composition and thickness do not change where they should be constant. This may sound trivial but deposition uniformity is never a given using such a directional deposition technique as PLD. In Figure S5 are

represented the intensity of photons emitted from Zr, Ca and Ir elements under electron bombardment while sweeping the e-beam probe (10  $\mu\text{m}$  diameter) along the vertical arrow. Along this vertical arrow, constant

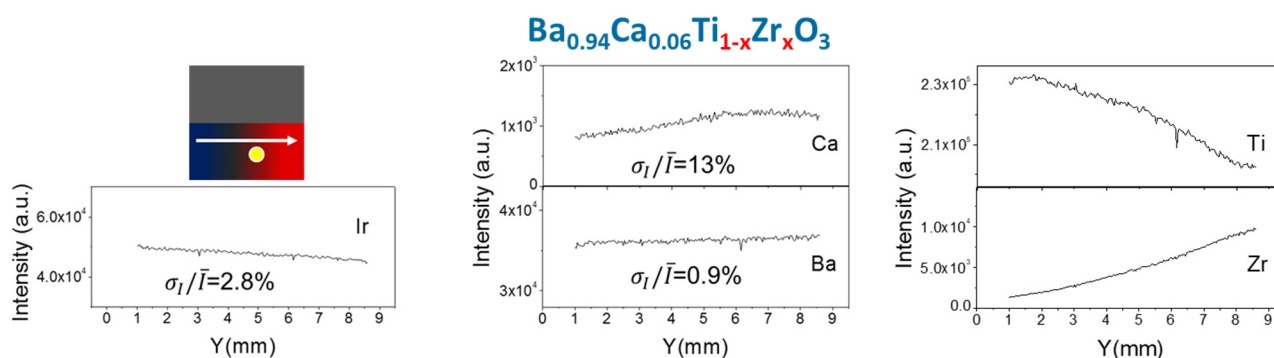


**Figure S5.** (a) WDS signals coming from Zr, Ca and Ir along the white arrow (left) where a constant composition and thickness of BCTZ is targeted.

BCTZ composition and thickness is intended. The small relative intensity variations ( $\sigma_I/\bar{I}$ ) for Ir, Zr and Ca shown in Figure S5 implies a good homogeneity of both the composition and thickness of BCTZ and IrO<sub>2</sub> layers. The higher variation for Ca correlates to its small signal amplitude relative to its small weight proportion within the probed volume.

### 3.2. Thickness homogeneity and composition variation along the gradient

Along the gradient direction, the absorption rates of the photons emitted by the elements are expected to slightly vary within the BCTZ layer as its composition evolves. Nevertheless, the Zr and Ti WDS signals showed, as expected, an anti-correlated almost linear continuous variation (see Figure S6), while the Ba and Ca signals showed little variation (Figure S6). A quantification of the BCTZ composition was achieved in one location of the library using the commercial software STRATAGEM. Photon absorptions are self-consistently calculated within each layers vs acceleration voltage and compared to the WDS signals obtained for a set of acceleration voltages.



**Figure S6.** Schematic (top left) of the 6% Ca library with the WDS scanning line (white arrow) and the location for quantitative measurement (yellow spot) together with the WDS signals coming from Ir, Ca, Ba, Ti, and Zr along the scan.

Assuming an oxygen stoichiometric formula  $\text{Ba}_x\text{Ca}_y\text{Ti}_z\text{Zr}_t\text{O}_3$  and no conditions on  $x$ ,  $y$ ,  $z$  and  $t$ , the extracted composition was  $\text{Ba}_{0.91}\text{Ca}_{0.08}\text{Ti}_{0.87}\text{Zr}_{0.14}\text{O}_3$ , close to the nominal  $\text{Ba}_{0.94}\text{Ca}_{0.06}\text{Ti}_{0.845}\text{Zr}_{0.155}\text{O}_3$ . Note that the total self-consistently extracted atomic composition for the A and B site ( $\text{A}_{0.99}\text{B}_{1.01}\text{O}_3$ ) are very close to unity.