# Supporting Information

# High permittivity (1-*x*)$Ba(Zr_{0.2}Ti_{0.8})O_3$ – *x*$(Ba_{0.7}Ca_{0.3})TiO_3$ (*x* = 0.45) epitaxial thin films with nanoscale phase fluctuations

***Nicu D. Scarisoreanu[1*], Floriana Craciun[2], Antoniu Moldovan[1], Valentin Ion[1] , Ruxandra Birjega[1], Corneliu Ghica[3], Raluca F. Negrea[3], Maria Dinescu[1]***

[1]National Institute for Laser, Plasma and Radiation Physics, 409 Atomistilor, 077125 Magurele, Romania

[2]CNR-ISC, Istituto dei Sistemi Complessi, Area della Ricerca di Roma-Tor Vergata, Via del Fosso del Cavaliere 100, I-00133, Rome, Italy

[3]National Institute of Materials Physics, 105 bis Atomistilor, 077125 Magurele, Romania

E-mail: nicu.scarisoreanu@inflpr.ro

**Contents:**

Dielectric constant and loss of used substrates.

Temperature dependence of $SrTiO_3$ dielectric constant.

Comparison with similar results reported on lead-free ferroelectric films.

References.

***Dielectric constant and loss of the substrates***

The dielectric constant and loss of the STO and SLAO substrates were obtained by measurements on interdigital electrodes deposited on the surfaces. The values were extracted by using the method described in the main text. The results are shown in Figure S1. The dielectric constant of STO varies between about 300 and 310 in the frequency range 1 kHz-1 MHz, while tan δ is about 0.005, very similar to the datasheet values given by the producer.

Also the measured dielectric constant of SLAO substrate is similar to the value given by the producer.

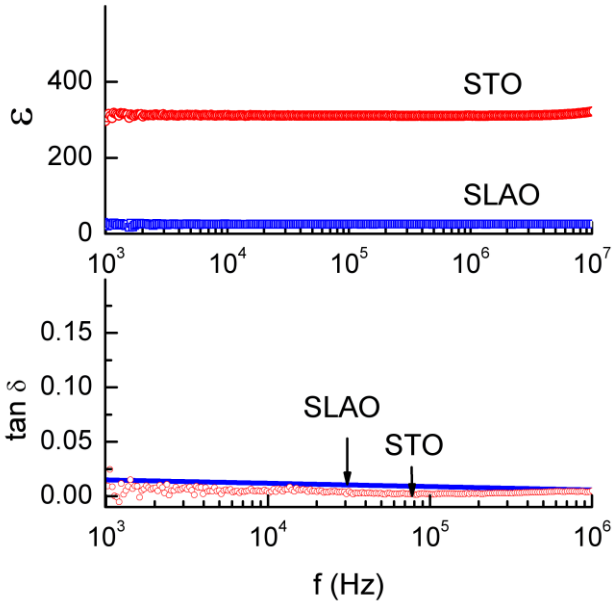


Figure S1. Dielectric constant and loss of substrates, measured with interdigital electrodes.

***Temperature dependence of $SrTiO_3$ dielectric constant***

STO is a quantum paraelectric with a very low transition temperature [1]. The variation of dielectric constant with temperature was obtained from the Curie-Weiss law,

$$\varepsilon(T) = \frac{C}{T - T_c} \tag{1}$$

where C is the Curie-Weiss constant and $T_c$ is the critical temperature. For STO, $C \approx 8\times10^4$ K and $T_c \approx 35$ K were experimentally determined in Ref. [1]. The results obtained by employing Eq. (1) are shown in Figure S2.

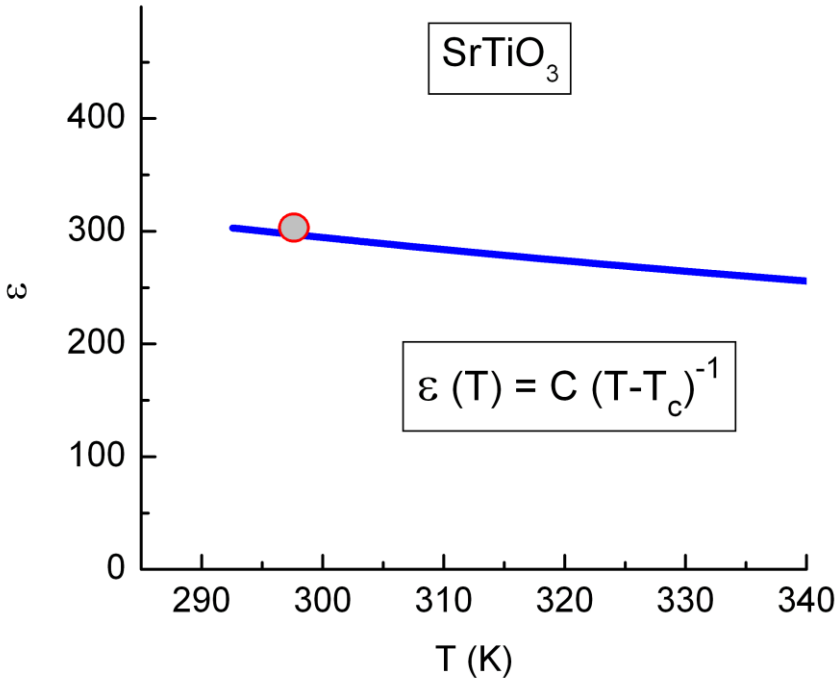


Figure S2. Calculated temperature dependence of the STO substrate's dielectric constant. The displayed point represents the value measured at 1 kHz on STO substrate with interdigital electrodes.

***Comparison with similar results reported on lead-free ferroelectric films***

The dielectric constant and loss of the BCZT/STO film were compared with other results reported in the literature for lead-free ferroelectric films obtained by different methods. The results are shown in Table S1.

Table S1. Comparison with dielectric results reported in the literature on lead-free ferroelectric films.

| Film Composition | Deposition method | Substrate | Thickness (nm) | Structure | Dielectric constant (300 K) | Tan d | Ref |
|---|---|---|---|---|---|---|---|
| BCZT 45 | PLD | STO | 175 | Epitaxial (001) oriented | 3150 | 0.008 | This work |
| BCZT 50 | PLD | Pt/Si | 600 | Polycrystalline (111) oriented | 1010 | | [2] |
| BCZT 45 | Sol-gel | Pt/Si | 400 | Polycrystalline Random orient. | 444 | 0.027 | [3] |
| BCZT 50 | Sol-gel | Pt/Si | 400 | Polycrystalline Random orient. | 377 | 0.022 | [3] |
| BCZT 55 | Sol-gel | Pt/Si | 400 | Polycrystalline Random orient. | 462 | 0.028 | [3] |
| NBT-BT 6 | Sol-gel | Pt/Si | 140 | Polycrystalline Random orient | 400 | 0.01 | [4] |
| NBT-BT 6 | Sol-gel | Pt/Si | 300 | Polycrystalline Random orient | 850 | 0.05 | [5] |
| NBT-BT 6 | PLD | Pt/Si | 450 | Polycrystalline Random orient | 1000 | 0.05 | [6] |

***References***

1. Müller, K. A.; Burkard, H. $SrTiO_3$: An Intrinsic Quantum Paraelectric Below 4 K. *Phys. Rev. B* **1979**, 19, 3593-3602.

2. Piorra, A.; Petraru, A.; Kohlstedt, H.; Wuttig, M.; Quandt, E. Piezoelectric Properties of 0.5(Ba0.7Ca0.3TiO3) – 0.5[Ba(Zr0.2Ti0.8)O3] Ferroelectric Lead-free Laser Deposited Thin Films. *J. Appl. Phys.* **2011**, 109, 104101- 104101-4.

3. Lin, Y.; Wu, G.; Qin, N.; Bao, D. Structure, Dielectric, Ferroelectric, and Optical Properties of (1 − x)Ba(Zr0.2Ti0.8)O3 − x(Ba0.7Ca0.3)TiO3 Thin Films Prepared by Sol–Gel Method. *Thin Solid Films* **2012**, 520, 2800-2804.

4. Alonso-Sanjosé, D.; Jimenez, R.; Bretos, I.; Calzada, M.L. Lead-free Ferroelectric $(Na_{1/2}Bi_{1/2})$-$BaTiO_3$ Thin Films in the Morphotropic Phase Boundary Composition: Solution Processing and Properties. *J. Am. Ceram. Soc.* **2009**, 92, 2218-2225.

5. Guo, Y.; Li, M.; Zhao, W.; Akai, D.; Sawada, K.; Ishida, M.; Gu, M. Ferroelectric and Pyroelectric Properties of $(Na_{0.5}Bi_{0.5})$-$BaTiO_3$ Based Trilayered Thin Films. *Thin Solid Films* **2009**, 517, 2974-2978.

6. Andrei, A.; Scarisoreanu, N.D.; Birjega, R.; Dinescu, M.; Stanciu, G.; Craciun, F.; Galassi, C. Pulsed Laser Deposition of Lead-free $(Na_{0.5}Bi_{0.5})_{1-x}$-$Ba_xTiO_3$ Ferroelectric Thin Films with Enhanced Dielectric Properties. *Appl. Surf. Sci.* **2013**, 278, 162-165.