

Table S1. Experimental parameters for X-ray powder diffraction of BZT, BLaZT and BSmZT powders.

<b>Crystallographic data</b>			
Chemical formula	BZT	BSmZT	BLaZT
Crystal system	Cubic	Cubic	Cubic
Space group	<i>Pm<math>\bar{3}m</math></i>	<i>Pm<math>\bar{3}m</math></i>	<i>Pm<math>\bar{3}m</math></i>
a (Å)	4.18061(11)	4.17226(11)	4.17882(12)
Volume (Å <sup>3</sup> )	73.067(3)	72.630(3)	72.973(4)
Z	1	1	1
Density (g/cm <sup>3</sup> )	6.002	6.0873	6.1179
Crystallite size (µm)	0.126	0.109	0.123
<b>Data collection</b>			
Temperature (°C)	25	25	25
CuKα Radiations (Å)	1.5406	1.5406	1.5406
Measuring range (°)	10 ≤ 2θ ≤ 120	10 ≤ 2θ ≤ 120	10 ≤ 2θ ≤ 120
Step (2θ)	0.015	0.015	0.015
<b>Rietveld data</b>			
Program	Jana 2006	Jana 2006	Jana 2006
Profile fonction	Pseudo-Voigt	Pseudo-Voigt	Pseudo-Voigt
Caglioti parameters	U = 0.051(5)	U = 0.038(6)	U = 0.018(2)
	V = -0.055(4)	V = -0.030(8)	V = -0.026(9)
	W = 0.037(2)	W = 0.024(4)	W = 0.029(1)
Rp (%)	6.16	6.20	6.26
Rwp (%)	8.43	8.45	8.86
GOF	1.31	1.35	1.49

Table S2. Refined structural parameters for BZT, BLaZT and BSmZT powder from X-ray diffraction data.

Compound	Wyckoff position	Atom	x	y	z	Uiso (Å)	Occupies
BZT	1a	Ba	0.5	0.5	0.5	0.0189(5)	0.962(19)
	1b	Ti/Zr	0	0	0	0.0157(4)	0.17(3)/0.83(3)
	3c	O	0.5	0	0	0.0120(1)	1
BLaZT	1a	Ba/La	0.5	0.5	0.5	0.0125(9)	0.85(5)/ 0.12(5)
	1b	Ti/Zr	0	0	0	0.0095(12)	0.11(2)/ 0.89(2)
	3c	O	0.5	0	0	0.0091(15)	1
BSmZT	1a	Ba	0.5	0.5	0.5	0.0101(9)	0.919(5)/0.048(5)
	1b	Ti/Zr	0	0	0	0.0053(12)	0.14 (1)/0.86 (1)
	3c	O	0.5	0	0	0.0135(18)	1

Table S3. Selected bond distances (Å) and angles (°) for BZT, BLaZT and BSmZT powder from X-ray diffraction data.

Bond distances (Å) and angles (°)	BZT	BSmZT	BLaZT
Ti/Zr–O	2.09015(12)	2.08596(11)	2.08904(13)
Ba/La–O	2.95592(12)	2.94999(11)	2.95434(13)
3×O1–Ti/Zr–O1	180.0(5)	180.0(5)	180.0(5)
12×O1–Ti/Zr–O1	90.000(2)	90.000(2)	90.0000(2)
6×O1–Ba/La–O1	180.0(5)	180.0(5)	180.0(5)
12×O1–Ba/La–O1	90.000(2)	90.000(2)	90.000(2)
Ti/Zr–O–Ti/Zr	180.0(5)	180.0(5)	180.0(5)
4xBa/La–O–Ba/La	90.000(2)	90.000(2)	90.000(2)
2xBa/La–O–Ba/La	180.0(5)	180.0(5)	180.0(5)
8xTi/Zr–O–Ba/La	90.000(1)	90.000(1)	90.000(1)

Table S4. Equivalent circuit electrical parameters obtained from a complex impedance spectrum for BZT, BLaZT and BSmZT ceramics.

	T (°C)	R <sub>g</sub> (MΩ)	Q <sub>g</sub> (nF.s <sup>α-1</sup> )	α <sub>g</sub>	R <sub>gb</sub> (MΩ)	Q <sub>gb</sub> (nF.s <sup>α-1</sup> )	α <sub>gb</sub>
BZT	320	86.96	0.191	0.987	-----	-----	----
	330	37.88	0.192	0.987	-----	-----	----
	340	18.72	0.197	0.985	-----	-----	----
	350	12.09	0.202	0.984	-----	-----	----
	360	8.60	0.207	0.982	-----	-----	----
	370	6.24	0.214	0.980	-----	-----	----
	380	4.45	0.221	0.978	-----	-----	----
BSmZT	320	5.50	1.08	0.926	0.455	0.263	0.957
	330	4.73	1.17	0.922	0.374	0.269	0.955
	340	3.41	1.34	0.912	0.278	0.264	0.952
	350	2.57	1.49	0.906	0.216	0.263	0.949
	360	1.88	1.66	0.899	0.165	0.262	0.946
	370	1.53	1.76	0.896	0.137	0.261	0.945
	380	1.12	1.91	0.890	0.105	0.262	0.942
BLaZT	320	3.08	0.832	0.949	0.221	0.312	0.977
	330	1.91	0.920	0.945	0.162	0.311	0.977
	340	1.31	0.951	0.940	0.139	0.306	0.976
	350	0.875	1.069	0.937	0.129	0.297	0.976
	360	0.717	1.102	0.932	0.083	0.290	0.975
	370	0.551	1.152	0.930	0.069	0.304	0.974
	380	0.475	0.832	0.928	0.059	0.303	0.974

Table S5. Parameters obtained from Joncher's plot for BZT, BLaZT and BSmZT ceramics.

Compound	T (°C)	$\sigma_{DC}$ ( $\Omega.m$ ) <sup>-1</sup>	$A_1$ ( $\Omega^{-1} m^{-1} rad^{-s}$ )	$s_1$	$A_2$ ( $\Omega^{-1} m^{-1} rad^{-s}$ )	$s_2$
BZT	320	$4.38 \times 10^{-6} \pm 1.34 \times 10^{-7}$	$3.84 \times 10^{-9} \pm 5.86 \times 10^{-10}$	$0.68 \pm 0.03$	-----	-----
	330	$8.35 \times 10^{-6} \pm 3.07 \times 10^{-7}$	$4.53 \times 10^{-9} \pm 3.72 \times 10^{-10}$	$0.67 \pm 0.04$	-----	-----
	340	$1.45 \times 10^{-5} \pm 2.84 \times 10^{-6}$	$5.03 \times 10^{-9} \pm 4.58 \times 10^{-10}$	$0.66 \pm 0.03$	-----	-----
	350	$2.15 \times 10^{-5} \pm 5.76 \times 10^{-6}$	$5.28 \times 10^{-9} \pm 1.63 \times 10^{-10}$	$0.65 \pm 0.01$	-----	-----
	360	$2.95 \times 10^{-5} \pm 3.51 \times 10^{-6}$	$5.17 \times 10^{-9} \pm 7.14 \times 10^{-10}$	$0.65 \pm 0.01$	-----	-----
	370	$3.95 \times 10^{-5} \pm 4.62 \times 10^{-6}$	$5.73 \times 10^{-9} \pm 4.96 \times 10^{-10}$	$0.64 \pm 0.03$	-----	-----
	380	$4.48 \times 10^{-5} \pm 2.04 \times 10^{-6}$	$6.93 \times 10^{-9} \pm 6.35 \times 10^{-10}$	$0.63 \pm 0.02$	-----	-----
BSmZT	320	$1.30 \times 10^{-5} \pm 7.34 \times 10^{-6}$	$1.65 \times 10^{-8} \pm 2.86 \times 10^{-9}$	$0.74 \pm 0.03$	$1.35 \times 10^{-7} \pm 1.55 \times 10^{-8}$	$0.54 \pm 0.01$
	330	$1.65 \times 10^{-5} \pm 1.25 \times 10^{-6}$	$1.91 \times 10^{-8} \pm 1.33 \times 10^{-9}$	$0.79 \pm 0.03$	$1.42 \times 10^{-7} \pm 2.86 \times 10^{-8}$	$0.53 \pm 0.01$
	340	$2.40 \times 10^{-5} \pm 2.56 \times 10^{-6}$	$2.12 \times 10^{-8} \pm 2.76 \times 10^{-9}$	$0.84 \pm 0.04$	$1.56 \times 10^{-7} \pm 2.76 \times 10^{-8}$	$0.52 \pm 0.01$
	350	$3.07 \times 10^{-5} \pm 4.09 \times 10^{-6}$	$2.76 \times 10^{-8} \pm 3.56 \times 10^{-9}$	$0.87 \pm 0.04$	$1.88 \times 10^{-7} \pm 1.94 \times 10^{-8}$	$0.51 \pm 0.02$
	360	$4.01 \times 10^{-5} \pm 3.55 \times 10^{-6}$	$3.12 \times 10^{-8} \pm 1.71 \times 10^{-9}$	$0.90 \pm 0.03$	$2.68 \times 10^{-7} \pm 2.88 \times 10^{-8}$	$0.50 \pm 0.01$
	370	$4.94 \times 10^{-5} \pm 7.42 \times 10^{-6}$	$3.95 \times 10^{-8} \pm 2.82 \times 10^{-9}$	$0.93 \pm 0.02$	$3.10 \times 10^{-7} \pm 9.98 \times 10^{-8}$	$0.43 \pm 0.02$
	380	$6.11 \times 10^{-5} \pm 3.83 \times 10^{-6}$	$5.34 \times 10^{-8} \pm 1.25 \times 10^{-9}$	$0.95 \pm 0.03$	$4.77 \times 10^{-7} \pm 1.54 \times 10^{-8}$	$0.42 \pm 0.02$
BLaZT	320	$2.03 \times 10^{-5} \pm 3.46 \times 10^{-6}$	$2.76 \times 10^{-8} \pm 2.26 \times 10^{-9}$	$0.64 \pm 0.04$	$2.44 \times 10^{-7} \pm 2.36 \times 10^{-8}$	$0.49 \pm 0.01$
	330	$2.91 \times 10^{-5} \pm 3.11 \times 10^{-6}$	$4.65 \times 10^{-8} \pm 1.36 \times 10^{-9}$	$0.66 \pm 0.03$	$2.55 \times 10^{-7} \pm 2.75 \times 10^{-8}$	$0.47 \pm 0.01$
	340	$4.08 \times 10^{-5} \pm 2.53 \times 10^{-6}$	$4.95 \times 10^{-8} \pm 6.24 \times 10^{-9}$	$0.687 \pm 0.03$	$3.90 \times 10^{-7} \pm 2.03 \times 10^{-8}$	$0.45 \pm 0.008$
	350	$5.32 \times 10^{-5} \pm 3.24 \times 10^{-6}$	$6.75 \times 10^{-8} \pm 8.15 \times 10^{-9}$	$0.73 \pm 0.03$	$4.72 \times 10^{-7} \pm 2.79 \times 10^{-8}$	$0.45 \pm 0.009$
	360	$6.51 \times 10^{-5} \pm 5.84 \times 10^{-6}$	$9.41 \times 10^{-8} \pm 2.01 \times 10^{-9}$	$0.75 \pm 0.03$	$6.28 \times 10^{-7} \pm 3.97 \times 10^{-8}$	$0.44 \pm 0.009$
	370	$7.41 \times 10^{-5} \pm 7.35 \times 10^{-6}$	$2.73 \times 10^{-7} \pm 2.64 \times 10^{-8}$	$0.81 \pm 0.03$	$7.61 \times 10^{-7} \pm 4.73 \times 10^{-8}$	$0.43 \pm 0.009$
	380	$8.54 \times 10^{-5} \pm 6.05 \times 10^{-6}$	$3.69 \times 10^{-7} \pm 1.25 \times 10^{-8}$	$0.83 \pm 0.03$	$9.03 \times 10^{-7} \pm 1.01 \times 10^{-8}$	$0.40 \pm 0.01$