Evaluation of polymorphism and charge transport in a BaO–CaO–Ta_2O_5 perovskite phase diagram using TOF-neutron and synchrotron X-ray diffraction, the bond-valence method and impedance spectroscopy

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Electronic Supporting Information (ESI)

Table S1. Rietveld refinement of $Ba_3Ca_{1+x}Ta_{2-x}O_{9-3x/2}$ ($0 \leq x \leq 0.36$) prepared at 1000 °C, using monochromatic synchrotron X-ray diffraction data (λ = 1.321 Å).

$Ba_3CaTa_2O_9$ (*P-3m1*), 1000 °C, 12 h, wRp = 2.84%, Rp = 2.2%, χ^2 = 1.299, a = b = 5.917(2) Å, c = 7.2482(2) Å				
Atom	**Position**	**Wyckoff position**	**Occupancy**	**100*Uiso**
Ba	0, 0, 0	*1a*	1	0.373(4)
Ba	0.3333, 0.6667, 0.6672(1)	*2d*	1	0.373(4)
Ta	0.3333, 0.6667, 0.1723(2)	*2d*	0.9132(4)	0.683(8)
Ca	0.3333, 0.6667, 0.1723(2)	*2d*	0.0868(4)	0.683(8)
Ta	0, 0, 0.5	*1b*	0.1736(3)	0.683(7)
Ca	0, 0, 0.5	*1b*	0.8264(3)	0.683(7)
O	0.5, 0, 0	*3e*	1	0.521(2)
O	0.1354(3), 0.8646(3), 0.3322(3)	*6i*	1	0.521(2)
$Ba_3Ca_{1.09}Ta_{1.91}O_{8.865}$ (*P-3m1*), 1000 °C, 12 h, wRp = 2.2%, Rp = 1.81%, χ^2 = 0.4629, a = b = 5.922(3) Å, c = 7.2563(3) Å				
Ba	0, 0, 0	*1a*	1	0.785(8)
Ba	0.3333, 0.6667, 0.663(2)	*2d*	1	0.785(8)
Ta	0.3333, 0.6667, 0.1794(3)	*2d*	0.7671(2)	0.873(4)
Ca	0.3333, 0.6667, 0.1794(5)	*2d*	0.2329(2)	0.873(4)
Ta	0, 0, 0.5	*1b*	0.3757(1)	1.376(6)
Ca	0, 0, 0.5	*1b*	0.6243(1)	1.376(6)

O	0.5, 0, 0	*3e*	0.985	1.02 (2)
O	0.1507(7), 0.8493(7), 0.2942(7)	*6i*	0.985	1.02(2)
$Ba_3Ca_{1.18}Ta_{1.82}O_{8.73}$ (*P-3m1*), 1000 ºC, 12 h, wRp = 4.77%, Rp = 3.91%, χ^2 = 3.153, a = b = 5.919(8) Å, c = 7.2520(8) Å				
Ba	0, 0, 0	*1a*	1	0.651(7)
Ba	0.3333, 0.6667, 0.663(3)	*2d*	1	0.651(7)
Ta	0.3333, 0.6667, 0.1693(4)	*2d*	0.8065(5)	0.332(4)
Ca	0.3333, 0.6667, 0.1693(4)	*2d*	0.1935(5)	0.332(4)
Ta	0, 0, 0.5	*1b*	0.2071(3)	0.303(3)
Ca	0, 0, 0.5	*1b*	0.7929(3)	0.303(3)
O	0.5, 0, 0	*3e*	0.97	0.231(8)
O	0.1685(6), 0.8315(6), 0.3433(6)	*6i*	0.97	0.231(8)
$Ba_3Ca_{1.27}Ta_{1.73}O_{8.595}$ (*P-3m1*), 1000 ºC, 12 h, wRp = 3.98%, Rp = 2.66%%, χ^2 = 1.665, a = b = 5.909(7) Å, c = 7.2218(7) Å				
Ba	0, 0, 0	*1a*	1	0.913(7)
Ba	0.3333, 0.6667, 0.663(2)	*2d*	1	0.913(7)
Ta	0.3333, 0.6667, 0.1703(4)	*2d*	0.8004(5)	0.785(9)
Ca	0.3333, 0.6667, 0.1703(4)	*2d*	0.1996(5)	0.785(9)
Ta	0, 0, 0.5	*1b*	0.1292(3)	0.578(6)
Ca	0, 0, 0.5	*1b*	0.8708(3)	0.578(6)
O	0.5, 0, 0	*3e*	0.955	0.879(8)
O	0.1324(6), 0.8675(6), 0.3681(6)	*6i*	0.955	0.879(8)
$Ba_3Ca_{1.36}Ta_{1.64}O_{8.415}$ (*P-3m1*), 1000 ºC, 12 h, wRp = 5.90%, Rp = 3.67%%, χ^2 = 6.702, a = b = 5.925(9) Å, c = 7.2554(9) Å				
Ba	0, 0, 0	*1a*	1	0.865(8)
Ba	0.3333, 0.6667, 0.663(9)	*2d*	1	0.865(8)
Ta	0.3333, 0.6667, 0.1703(8)	*2d*	0.7245(9)	0.779(4)
Ca	0.3333, 0.6667, 0.1703(8)	*2d*	0.2755(9)	0.779(4)
Ta	0, 0, 0.5	*1b*	0.2309(4)	0.497(3)
Ca	0, 0, 0.5	*1b*	0.7691(4)	0.497(3)
O	0.5, 0, 0	*3e*	0.935	0.971(7)
O	0.1223(6), 0.8777(6), 0.4281(6)	*6i*	0.935	0.971(7)

Table S2. Rietveld refinement of $Ba_3Ca_{1+x}Ta_{2-x}O_{9-3x/2}$ ($0 \leq x \leq 0.36$) prepared at 1100 ºC, using TOF-Neutron diffraction data.

$Ba_3CaTa_2O_9$ (*P-3m1*), 1100 ºC, 12 h, wRp = 2.97%, Rp = 9.34%, χ^2 = 1.275, a = b = 5.90141(8) Å, c = 7.2628(2) Å				
Atom	**Position**	**Wyckoff position**	**Occupancy**	**100*Uiso**
Ba	0, 0, 0	*1a*	1	0.734 (6)
Ba	0.3333, 0.6667, 0.6672(3)	*2d*	1	0.734(6)
Ta	0.3333, 0.6667, 0.1684(6)	*2d*	0.9132	0.255(6)
Ca	0.3333, 0.6667, 0.1684(6)	*2d*	0.0868	0.255(6)
Ca	0, 0, 0.5	*1b*	0.8264	0.807(5)
Ta	0, 0, 0.5	*1b*	0.1736	0.807(5)
O	0.5, 0, 0	*3e*	1	1.385(2)
O	0.1748(3), 0.8252(6), 0.3159(4)	*6i*	1	1.385(2)
$Ba_3Ca_{1.09}Ta_{1.91}O_{8.865}$ (*P-3m1*), 1100 ºC, 12 h, wRp = 2.94%, Rp = 5.65%, χ^2 = 4.599, a = b = 5.926(5) Å, c = 7.3028(7) Å				
Ba	0, 0, 0	*1a*	1	1.309(8)
Ba	0.3333, 0.6667, 0.663(2)	*2d*	1	1.309(8)
Ta	0.3333, 0.6667, 0.1740(3)	*2d*	0.955(4)	0.368(4)
Ca	0.3333, 0.6667, 0.1740(3)	*2d*	0.045(4)	0.368(4)
Ca	0, 0, 0.5	*1b*	1	0.598(6)
O	0.5, 0, 0	*3e*	0.985	0.781(2)
O	0.1571(4), 0.8429(2), 0.3491(7)	*6i*	0.985	0.781(2)
$Ba_3Ca_{1.18}Ta_{1.82}O_{8.73}$ (*P-3m1*), 1100 ºC, 12 h, wRp = 2.78%, Rp = 4.51%, χ^2 = 5.207, a = b = 5.929(5) Å, c = 7.2505(4) Å				
Ba	0, 0, 0	*1a*	1	1.019(8)
Ba	0.3333, 0.6667, 0.663(8)	*2d*	1	1.019(8)
Ta	0.3333, 0.6667, 0.1740(9)	*2d*	0.91(4)	0.638(7)
Ca	0.3333, 0.6667, 0.1740(9)	*2d*	0.09(4)	0.638(7)
Ca	0, 0, 0.5	*1b*	1	0.252(3)
O	0.5, 0, 0	*3e*	0.97	1.71(2)
O	0.1601(5), 0.8398(8), 0.3410(9)	*6i*	0.97	1.71(2)
$Ba_3Ca_{1.27}Ta_{1.73}O_{8.595}$ (*P-3m1*), 1100 ºC, 12 h, wRp = 2.51%, Rp = 4.58%, χ^2 = 4.532, a = b = 5.930(3) Å, c = 7.257(6) Å				
Ba	0, 0, 0	*1a*	1	1.232(1)
Ba	0.3333, 0.6667, 0.663(8)	*2d*	1	1.232 (1)
Ta	0.3333, 0.6667, 0.1740(9)	*2d*	0.865(5)	0.638(7)
Ca	0.3333, 0.6667, 0.1740(9)	*2d*	0.135(5)	0.638(7)
Ca	0, 0, 0.5	*1b*	1	0.243(6)
O	0.5, 0, 0	*3e*	0.955	0.389(4)
O	0.1580(3), 0.8420(7), 0.3422(9)	*6i*	0.955	0.389(4)

$Ba_3Ca_{1.09}Ta_{1.91}O_{8.865}$ (*Fm-3m*), 1100 ºC, 12 h, wRp = 2.94%, Rp = 5.65%, χ^2 = 4.599, a = b = c = 8.3946(2) Å				
Ba	0.25, 0.25, 0.25	*8c*	1	0.859(7)
Ta	0.5, 0.5, 0.5	*4b*	0.8788(6)	0.579(4)
Ca	0.5, 0.5, 0.5	*4b*	0.1212(6)	0.579(4)
Ta	0, 0, 0	*4a*	0.3942(5)	0.331(2)

Ca	0, 0, 0	*4a*	0.6058(5)	0.331(2)
O	0.2544(5), 0, 0	*24e*	0.985	1.229(5)
$Ba_3Ca_{1.18}Ta_{1.82}O_{8.73}$ (*Fm-3m*), 1100 ºC, 12 h, wRp = 2.78%, Rp = 4.51%, χ^2 = 5.207, a = b = c = 8.444(6) Å				
Ba	0.25, 0.25, 0.25	*8c*	1	0.502(8)
Ta	0.5, 0.5, 0.5	*4b*	1	0.674(4)
Ta	0, 0, 0	*4a*	0.213(2)	0.583(3)
Ca	0, 0, 0	*4a*	0.787(2)	0.583(3)
O	0.2724(5), 0, 0	*24e*	0.98	0.424(8)
$Ba_3Ca_{1.27}Ta_{1.73}O_{8.595}$ (*Fm-3m*), 1100 ºC, 12 h, wRp = 2.51%, Rp = 4.58%, χ^2 = 4.532, a = b = c = 8.5105(2) Å				
Ba	0.25, 0.25, 0.25	*8c*	1	1.204(7)
Ta	0.5, 0.5, 0.5	*4b*	0.153(4)	1.56(9)
Ca	0.5, 0.5, 0.5	*4b*	0.847(4)	1.56(9)
Ta	0, 0, 0	*4a*	1	0.434(5)
O	0.2294(5), 0, 0	*24e*	0.955	0.280(4)

Table S3. Rietveld refinement of $Ba_3Ca_{1+x}Ta_{2-x}O_{9-3x/2}$ ($0 \le x \le 0.36$) prepared at 1400 ^oC, using monochromatic synchrotron X-ray diffraction data (λ = 1.321 Å).

$Ba_3CaTa_2O_9$ (*P-3m1*), 1400 ^oC, 12 h, wRp = 5.49%, Rp = 3.83%, χ^2 = 0.4524, a = b = 5.919(3) Å, c = 7.292(3) Å				
Atom	**Position**	**Wyckoff position**	**Occupancy**	**100*Uiso**
Ba	0, 0, 0	*1a*	1	0.443(6)
Ba	0.3333, 0.6667, 0.6672(3)	*2d*	1	0.443(6)
Ta	0.3333, 0.6667, 0.1784(2)	*2d*	1	1.19(4)
Ca	0, 0, 0.5	*1b*	1	1.19(4)
O	0.5, 0, 0	*3e*	1	0.427(2)
O	0.1354(3), 0.8646(3), 0.3322(3)	*6i*	1	0.427(2)
$Ba_3Ca_{1.09}Ta_{1.91}O_{8.865}$ (*P-3m1*), 1400 ^oC, 12 h, wRp = 5.5%, Rp = 3.5%, χ^2 = 0.6333, a = b = 5.904(3) Å, c = 7.288(5) Å				
Ba	0, 0, 0	*1a*	1	0.307(8)
Ba	0.3333, 0.6667, 0.663(2)	*2d*	1	0.307(8)
Ta	0.3333, 0.6667, 0.1827(3)	*2d*	0.955(3)	0.451(4)
Ca	0.3333, 0.6667, 0.1827(3)	*2d*	0.045(3)	0.451(4)
Ca	0, 0, 0.5	*1b*	1	0.501(6)
O	0.5, 0, 0	*3e*	0.985	1.15 (2)
O	0.1461(2), 0.8539(8), 0.3281(2)	*6i*	0.985	1.15(2)
$Ba_3Ca_{1.18}Ta_{1.82}O_{8.73}$ (*P-3m1*), 1400 ^oC, 12 h, wRp = 4.94%, Rp = 3.81%, χ^2 = 3.322, a = b = 5.942(5) Å, c = 7.2597(4) Å				
Ba	0, 0, 0	*1a*	1	0.471(7)
Ba	0.3333, 0.6667, 0.663(3)	*2d*	1	0.471(7)
Ta	0.3333, 0.6667, 0.1751(4)	*2d*	0.91	0.547(7)
Ca	0.3333, 0.6667, 0.1751(4)	*2d*	0.09	0.547(7)
Ca	0, 0, 0.5	*1b*	1	0.398(3)
O	0.5, 0, 0	*3e*	0.97	1.71(2)
O	0.1176(6), 0.8823(4), 0.3507(3)	*6i*	0.97	1.71(2)
$Ba_3Ca_{1.27}Ta_{1.73}O_{8.595}$ (*P-3m1*), 1400 ^oC, 12 h, wRp = 8.32%, Rp = 4.87%, χ^2 = 4.222, a = b = 5.955(6) Å, c = 7.276(1) Å				
Ba	0, 0, 0	*1a*	1	0.227(1)
Ba	0.3333, 0.6667, 0.663(8)	*2d*	1	0.227(1)
Ta	0.3333(4), 0.6667(4), 0.1703(4)	*2d*	0.865(5)	1.502(9)
Ca	0.3333(4), 0.6667(4), 0.1703(4)	*2d*	0.135(5)	1.502(9)
Ca	0, 0, 0.5	*1b*	1	0.289(6)
O	0.5, 0, 0	*3e*	0.955	0.879(8)
O	0.1359(3), 0.8641(7), 0.2975(2)	*6i*	0.955	0.879(8)
$Ba_3Ca_{1.36}Ta_{1.64}O_{8.415}$ (*P-3m1*), 1400 ^oC, 12 h, wRp = 5.99%, Rp = 3.86%, χ^2 = 2.413, a = b = 5.917(3) Å, c = 7.2346(2) Å				
Ba	0, 0, 0	*1a*	1	0.433(3)
Ba	0.3333, 0.6667, 0.663(9)	*2d*	1	0.433(3)
Ta	0.3333, 0.6667, 0.1740(8)	*2d*	0.72 (2)	0.513(6)
Ca	0.3333, 0.6667, 0.1740(8)	*2d*	0.18(2)	0.513(6)
Ca	0, 0, 0.5	*1b*	1	0.235(3)
O	0.5, 0, 0	*3e*	0.935	0.476(7)
O	0.1481(3), 0.8519(8), 0.3160(9)	*6i*	0.935	0.476(7)

$Ba_3Ca_{1.09}Ta_{1.91}O_{8.865}$ (*Fm-3m*), 1400 ºC, 12 h, wRp = 5.5%, Rp = 3.5%, χ^2 = 0.6333, a = b = c = 8.403(3) Å				
Ba	0.25, 0.25, 0.25	*8c*	1	0.785(8)
Ta	0.5, 0.5, 0.5	*4b*	1	0.873(4)
Ta	0, 0, 0	*4a*	0.273(6)	1.001(4)
Ca	0, 0, 0	*4a*	0.727(6)	1.001(6)
O	0.2202(8), 0, 0	*24e*	0.985	0.579(6)
$Ba_3Ca_{1.18}Ta_{1.82}O_{8.73}$ (*Fm-3m*), 1400 ºC, 12 h, wRp = 4.94%, Rp = 3.81%, χ^2 = 3.322, a = b = c = 8.459(2) Å				
Ba	0.25, 0.25, 0.25	*8c*	1	0.502(8)
Ta	0.5, 0.5, 0.5	*4b*	1	0.726(4)
Ta	0, 0, 0	*4a*	0.213(2)	0.611 (3)
Ca	0, 0, 0	*4a*	0.787(2)	0.611(3)
O	02586(3), 0, 0	*24e*	0.97	0.726(8)
$Ba_3Ca_{1.27}Ta_{1.73}O_{8.595}$ (*Fm-3m*), 1400 ºC, 12 h, wRp = 8.32%, Rp = 4.87%, χ^2 = 4.222, a = b = c = 8.444(3) Å				
Ba	0.25, 0.25, 0.25	*8c*	1	0.815(7)
Ta	0.5, 0.5, 0.5	*4b*	0.153(4)	1.56(9)
Ca	0.5, 0.5, 0.5	*4b*	0.847(4)	1.56(9)
Ta	0, 0, 0	*4a*	1	1.42(8)
O	0.2697(5), 0, 0	*24e*	0.955	0.770(8)
$Ba_3Ca_{1.36}Ta_{1.64}O_{8.415}$ (*Fm-3m*), 1400 ºC, 12 h, wRp = 5.99%, Rp = 3.86%, χ^2 = 2.413, a = b = c = 8.4316(1) Å				
Ba	0, 0, 0	*8c*	1	0.572(3)
Ta	0.5, 0.5, 0.5	*4b*	1	0.82(4)
Ca	0, 0, 0	*4b*	0.91(2)	1.36(4)
Ta	0, 0, 0	*4a*	0.09(2)	1.36(4)
O	0.2482(1), 0, 0	*24e*	0.935	1.05(4)

Table S4. Rietveld refinement of $Ba_3Ca_{1+x}Ta_{2-x}O_{9-3x/2}$ ($0 \leq x \leq 0.36$) prepared at 1550 °C, using TOF-Neutron diffraction data.

$Ba_3CaTa_2O_9$ (*P-3m1*), 1550 °C, 12 h, wRp = 2.54%, Rp = 6.98%, χ^2 = 5.174, a = b = 5.90263(3) Å, c = 7.27439(8) Å				
Ba	0, 0, 0	*1a*	1	0.670(3)
Ba	0.3333, 0.6667, 0.6671(2)	*2d*	1	0.670(3)
Ta	0.3333, 0.6667, 0.1684(2)	*2d*	1	0.265(6)
Ca	0, 0, 0.5	*1b*	1	0.265(6)
O	0.5, 0, 0	*3e*	1	1.133(7)
O	0.1757(5), 0.8243(5), 0.3140(2)	*6i*	1	1.133(7)
$Ba_3Ca_{1.09}Ta_{1.91}O_{8.865}$ (*Fm-3m*), 1550 °C, 12 h, wRp = 4.62%, Rp = 8.37%, χ^2 = 14.32, a = b = c = 8.39421(5) Å				
Ba	0.25, 0.25, 0.25	*8c*	1	0.847(3)
Ta	0.5, 0.5, 0.5	*4b*	0.3201(8)	0.462(4)
Ca	0.5, 0.5, 0.5	*4b*	0.6799(8)	0.462(4)
Ta	0, 0, 0	*4a*	0.9529(8)	0.462(4)
Ca	0, 0, 0	*4a*	0.0471(8)	0.462(4)
O	0.2395(6), 0, 0	*24e*	0.985	1.213(8)
$Ba_3Ca_{1.18}Ta_{1.82}O_{8.73}$ (*Fm-3m*), 1550 °C, 12 h, wRp = 3.97%, Rp = 8.39%, χ^2 = 10.35, a = b = c = 8.4236(1) Å				
Ba	0.25, 0.25, 0.25	*8c*	1	1.06(3)
Ta	0.5, 0.5, 0.5	*4b*	1	0.451(9)
Ca	0, 0, 0	*4a*	0.787(7)	0.533(9)
Ta	0, 0, 0	*4a*	0.213(7)	0.533(8)
O	0.2613(3), 0, 0	*24e*	0.97	1.226(2)
$Ba_3Ca_{1.27}Ta_{1.73}O_{8.595}$ (*Fm-3m*), 1550 °C, 12 h, wRp = 4.73%, Rp = 8.67%, χ^2 = 17.13, a = b = c = 8.43722(4) Å				
Ba	0, 0, 0	*8c*	1	0.572(3)
Ta	0.5, 0.5, 0.5	*4b*	0.153	0.781(4)
Ca	0.5, 0.5, 0.5	*4b*	0.847	0.781(4)
Ta	0, 0, 0	*4a*	1	0.501(6)
O	0.2373(6), 0, 0	*24e*	0.955	1.242(7)

Table S5. Relative density of structural dependent BCT samples prepared at 1550 ^{o}C.

Composition	**Relative Density (%)**	**Phase**
BCT00	70.1	*P-3m1*
BCT09	72.9	*Fm-3m*
BCT18	78.8	*Fm-3m*
BCT27	85.7	*Fm-3m*
BCT36	89.9	*Fm-3m*
BCN18	**92.5**	***Fm-3m***

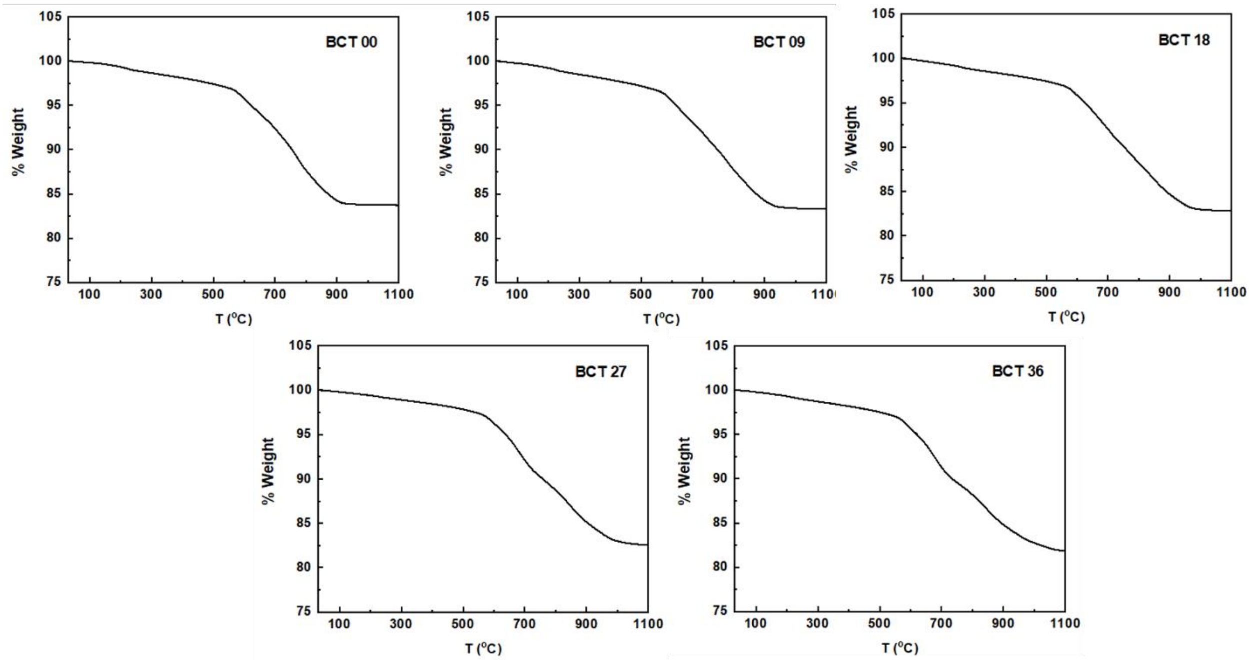

Figure S1. Thermogravimetric analysis (TGA) of $Ba_3Ca_{1+x}Ta_{2-x}O_{9-3x/2}$ ($0 \leq x \leq 0.36$) precursors heated in air from room temperature to 1100 °C.

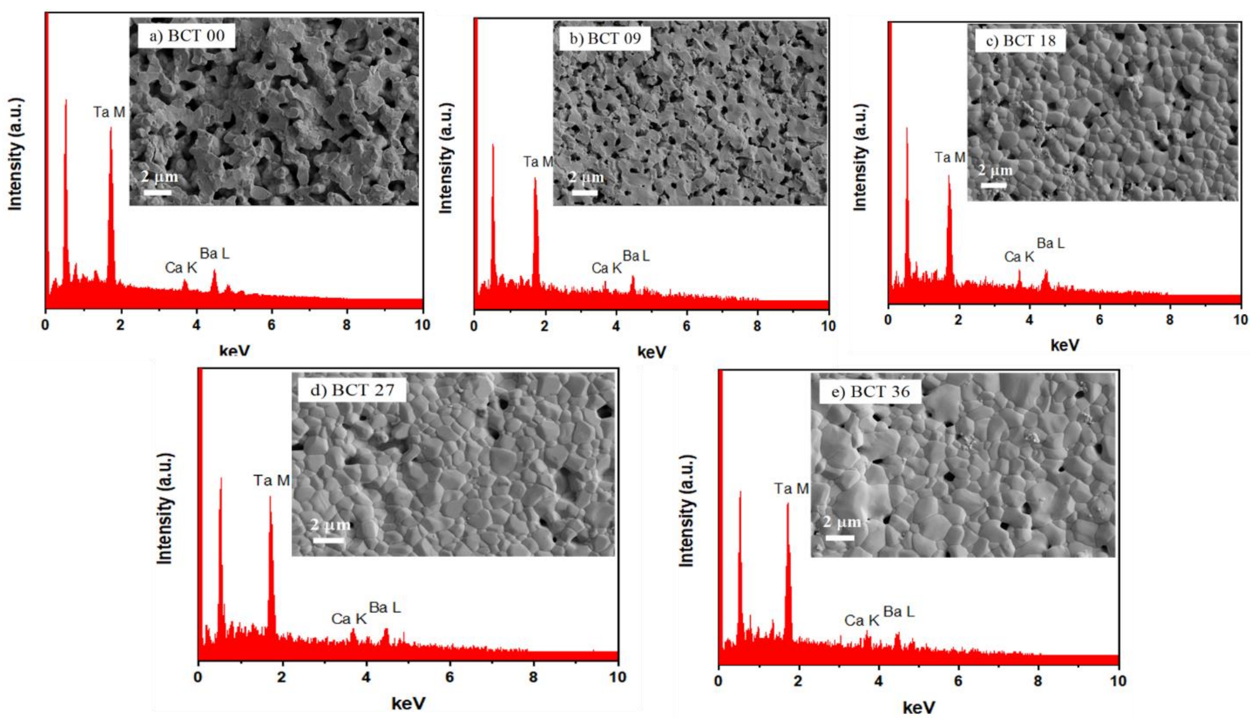

Figure S2. SEM and EDX images of $Ba_3Ca_{1+x}Ta_{2-x}O_{9-3x/2}$ ($0 \leq x \leq 0.36$) prepared at 1550 °C.

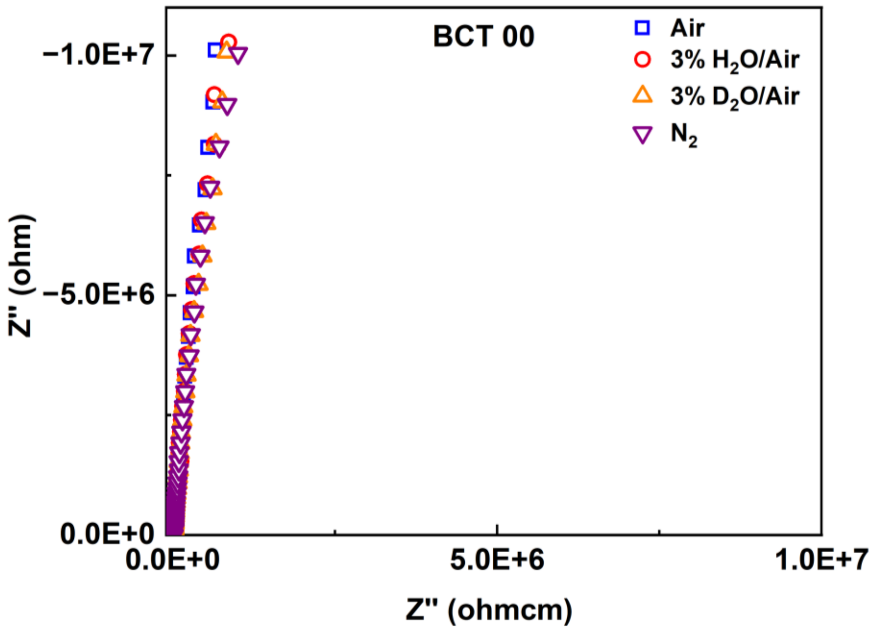

Figure S3. Nyquist plots at temperature 500 °C for $Ba_3CaTa_2O_9$ (BCT00) in air, 3% H_2O/air, 3% D_2O/air, and N_2. The samples for electrical conductivity measurements were prepared at 1550 °C for 24 h in air.

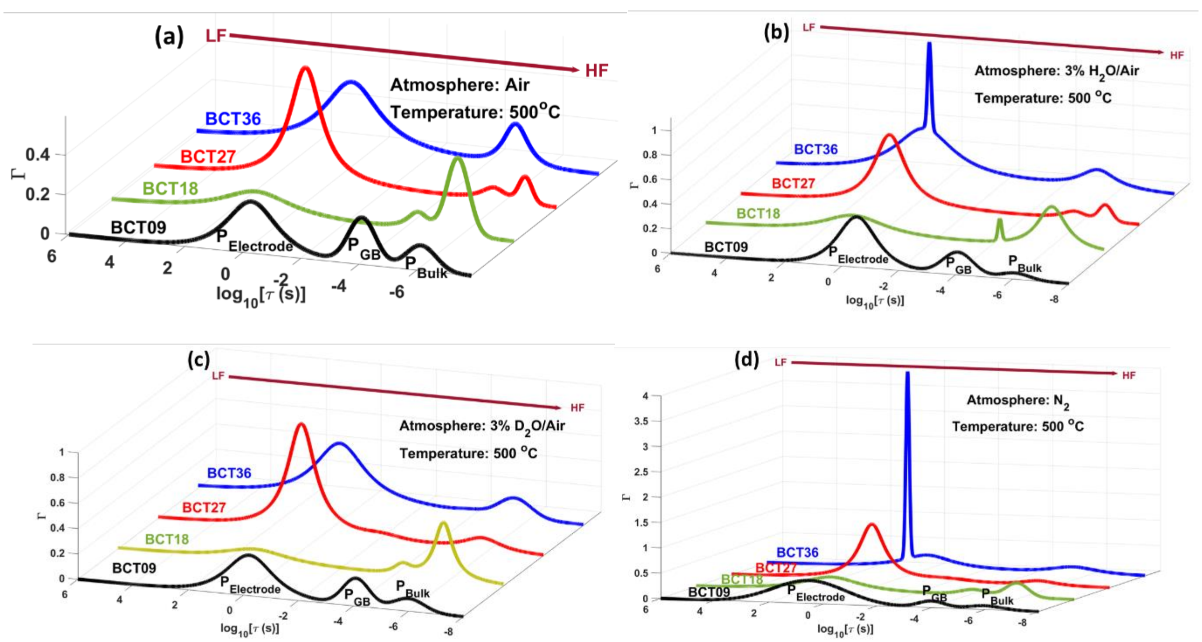

Figure S4. DFRT plots for $Ba_3Ca_{1+x}Ta_{2-x}O_{9-3x/2}$ ($0 \leq x \leq 0.36$) under (a) air, (b) 3% H_2O/Air, (c) 3% D_2O/air, and (d) N_2 at 500 °C showing presence of three peaks due to bulk, grain-boundary (GB), and electrode transport processes.