Supplementary Information

Pyrocatalytic Oxidation - Strong Size-Dependent Poling Effect on Catalytic Activity of Pyroelectric $BaTiO_3$ Nano- and Microparticles

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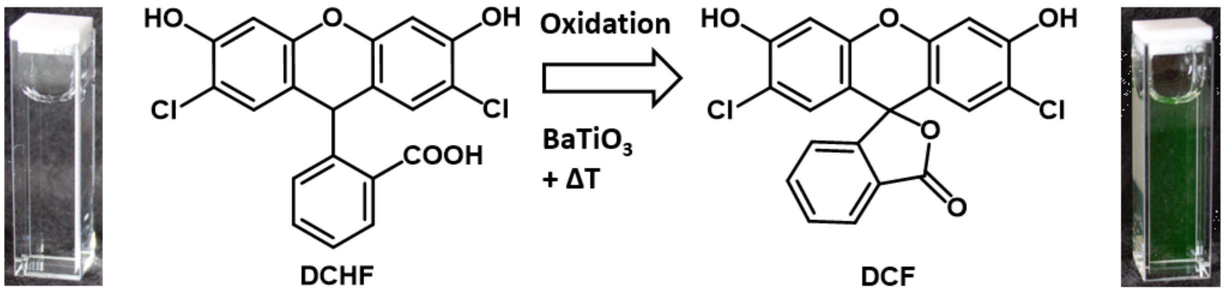
Number of pages: 9 Number of Figures: 8 Number of Tables: 3 Number of Schemes: 1

Scheme S.1: Pyrocatalytic oxidation of non-fluorescent 2',7'-dichlorodihydrofluorescein (DCHF) to fluorescent 2',7'-dichlorofluorescein (DCF).



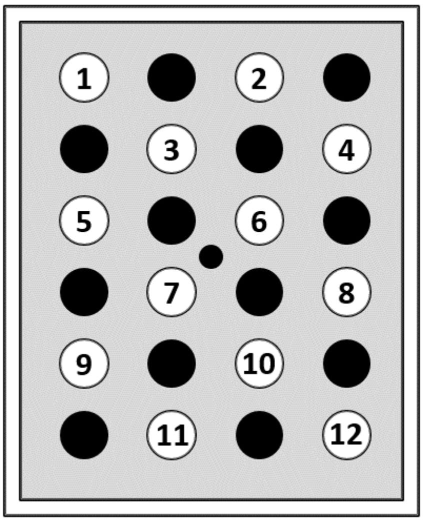


Figure S.1. Schematic sketch of the aluminium block of the thermomixer with 24 slots. In a typical experiment, up to 12 micro tubes were placed in every second slot (numbered slots).

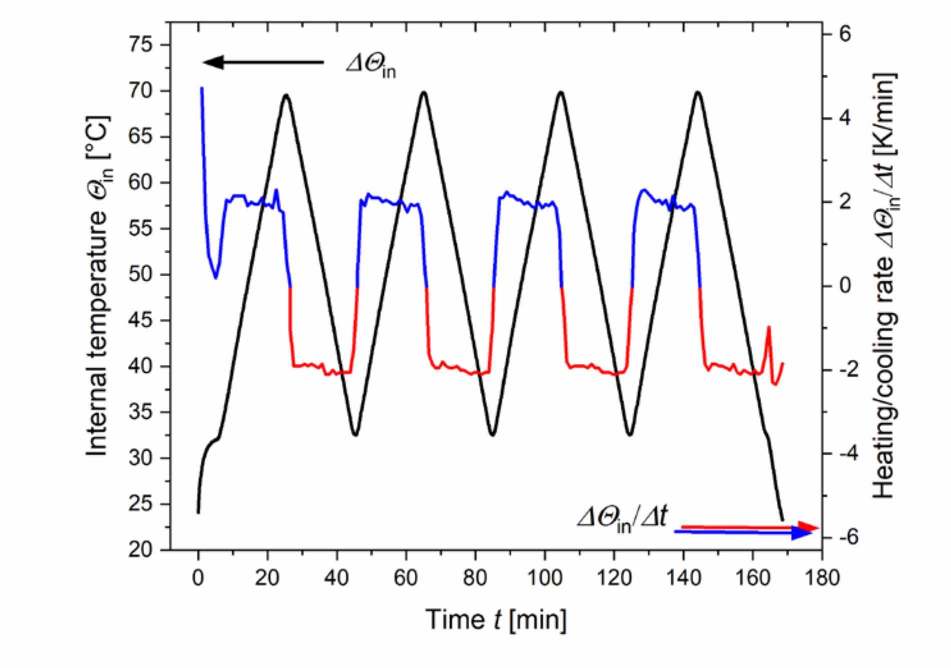


Figure S.2. Measured temperature inside the reaction vessel Θ_{in} over time t and corresponding heating/cooling rate $\Delta\Theta_{in}/\Delta t$ for the whole temperature program used in the DCHF-oxidation experiments. It consists of a 5 min equilibration phase at 32.5 °C followed by four full cycles and a 5 min cooling phase back to the starting temperature.

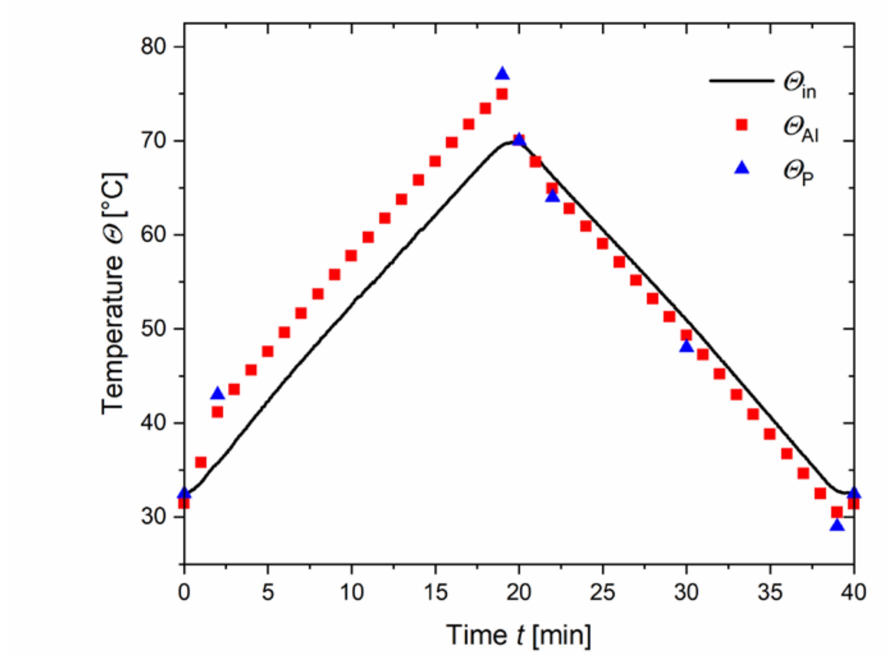


Figure S.3. Measured temperature inside the reaction vessel Θ_{in}, of the aluminium block of the thermoshaker Θ_{Al} and the preset temperature Θ_{P} over time t for one temperature cycle used in the DCHF-oxidation experiments.

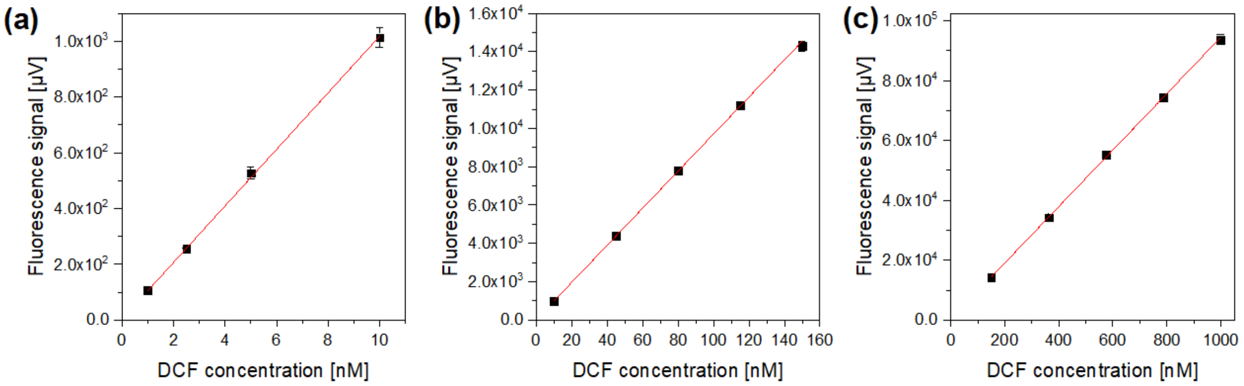


Figure S.4. Results and linear regression of external calibration of DCF with fluorescence spectroscopy in three concentration ranges: (a) 1 – 10 nM, (b) 10 – 150 nM, (c) 150 – 1000 nM.

Table S.1. Calibration parameters of the linear regression for the quantification of DCF via fluorescence spectroscopy.

Working range [nM]	*m* [µV/nM]	*n* [µV]	*LOD* [nM]	*LOQ* [nM]
1 - 10	100.8	10.0	0.15	0.5
10 - 150	95.3	105.4	1.19	3.6
150 - 1000	93.5	622.9	5.44	16.3

m: slope, *n*: intercept, *LOD*: limit of detection, *LOQ*: limit of quantification

Table S.2. Crystallographic data of Rietveld refinement for unpoled BT powders.

Sample	BT100		BT200		BT500	
RWP [%]	6.8		6.4		8.4	
goodness of fit	2.45		2.20		3.22	
compounds	$BaTiO_3$	$BaTiO_3$	$BaTiO_3$	$BaTiO_3$	$BaTiO_3$	$BaTiO_3$
crystal system	cubic	tetragonal	cubic	tetragonal	cubic	tetragonal
space group	$Pm\bar{3}m$	*P4mm*	$Pm\bar{3}m$	*P4mm*	$Pm\bar{3}m$	*P4mm*
lattice parameters						
a, *b* [Å]	4.0133(1)	4.0005(1)	4.0108(1)	3.9969(1)	4.0082(1)	3.9960(1)
c [Å]	4.0133(1)	4.0276(1)	4.0108(1)	4.0359(1)	4.0082(1)	4.0384(1)
c/a – 1 [%]	-	0.6774	-	0.9758	-	1.061
weight fraction [%]	38.2 ± 2.4	61.8 ± 2.4	18.0 ± 2.2	82.0 ± 2.2	8.7 ± 3.3	91.3 ± 3.3

BTX00: $BaTiO_3$ powder with X00 nm nominal particle size; RWP: residual weighted profile

Table S.3. Crystallographic data of Rietveld refinement for poled BT powders.

Sample	BT100		BT200		BT500	
RWP [%]	6.3		7.1		7.7	
goodness of fit	2.37		2.59		2.91	
compounds	$BaTiO_3$	$BaTiO_3$	$BaTiO_3$	$BaTiO_3$	$BaTiO_3$	$BaTiO_3$
crystal system	cubic	tetragonal	cubic	tetragonal	cubic	tetragonal
space group	$Pm\bar{3}m$	*P4mm*	$Pm\bar{3}m$	*P4mm*	$Pm\bar{3}m$	*P4mm*
lattice parameters						
a, *b* [Å]	4.0138(1)	4.0006(1)	4.0111(1)	3.9968(1)	4.0054(1)	3.9950(1)
c [Å]	4.0138(1)	4.0294(1)	4.0111(1)	4.0363(1)	4.0054(1)	4.0374(1)
c/a – 1 [%]	-	0.7199	-	0.9883	-	1.061
weight fraction [%]	33.3 ± 2.9	66.7 ± 2.9	18.1 ± 2.0	81.9 ± 2.0	8.0 ± 3.2	92.0 ± 3.2

BTX00: $BaTiO_3$ powder with X00 nm nominal particle size; RWP: residual weighted profile

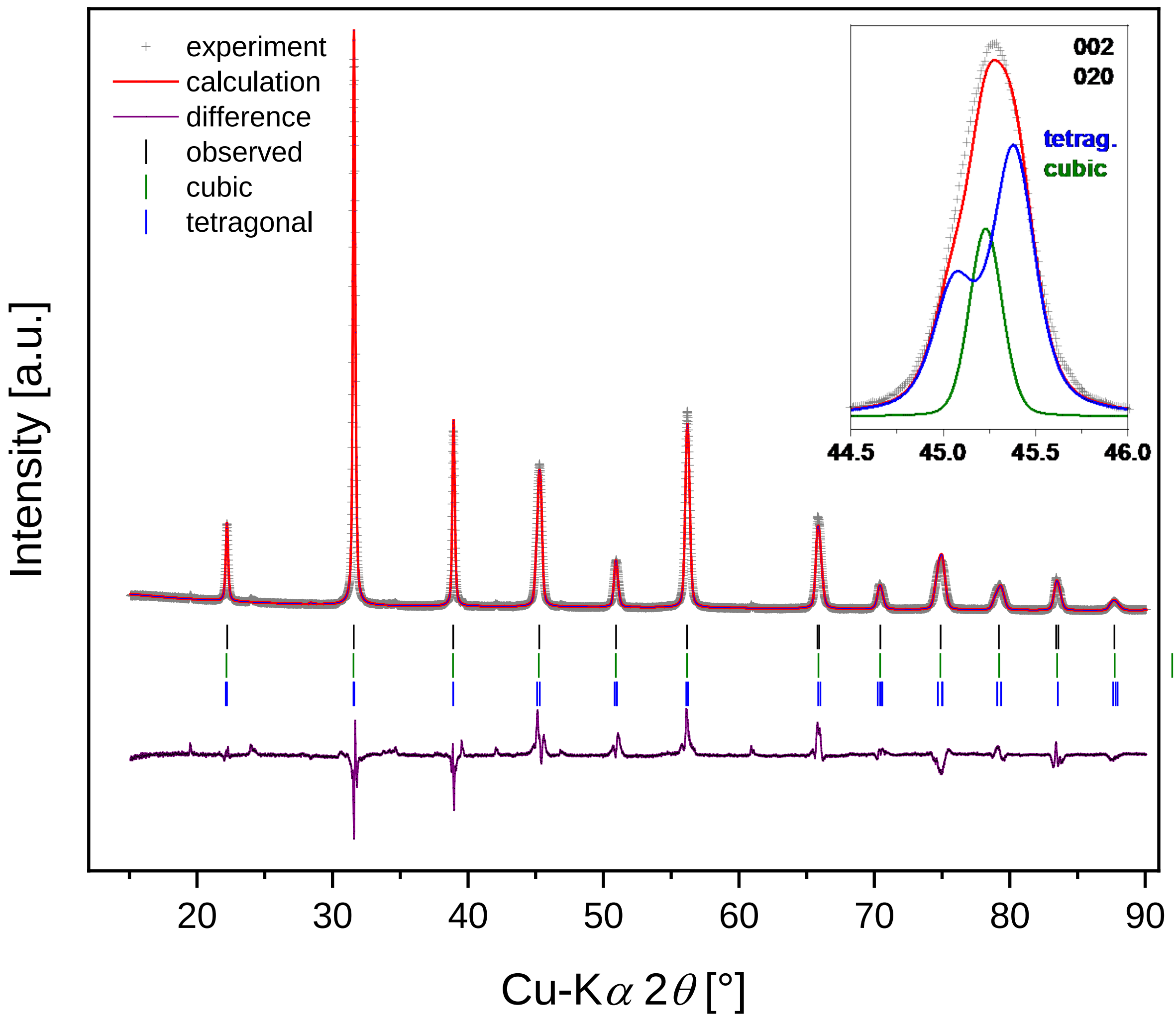


Figure S.5. Rietveld refinement results of unpoled $BaTiO_3$ powder with 100 nm nominal particle diameter (BT100). Inset shows composition of 002/020 reflection with respect to cubic and tetragonal fraction.

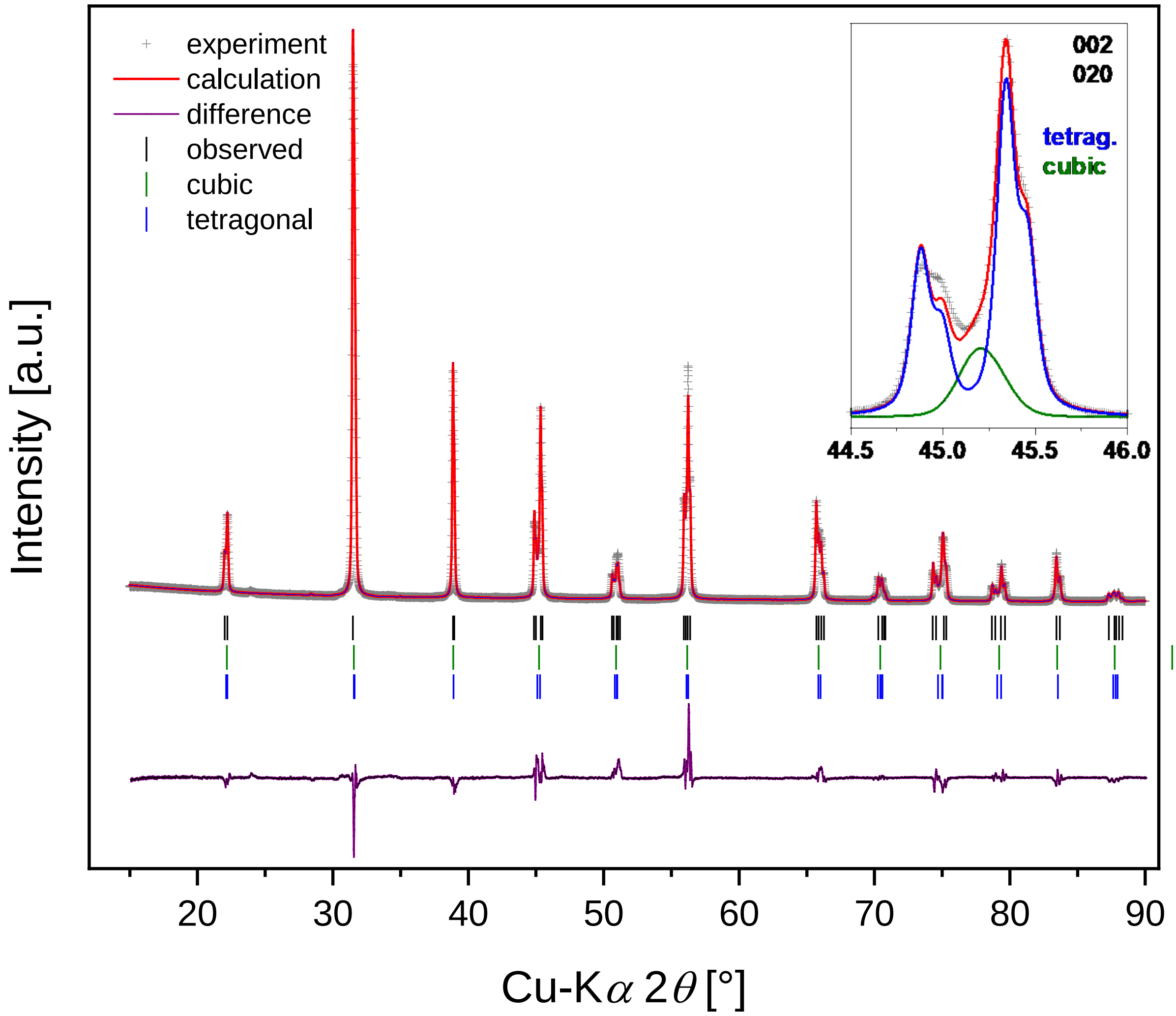


Figure S.6. Rietveld refinement results of unpoled $BaTiO_3$ powder with 200 nm nominal particle diameter (BT200). Inset shows composition of 002/020 reflection with respect to cubic and tetragonal fraction.

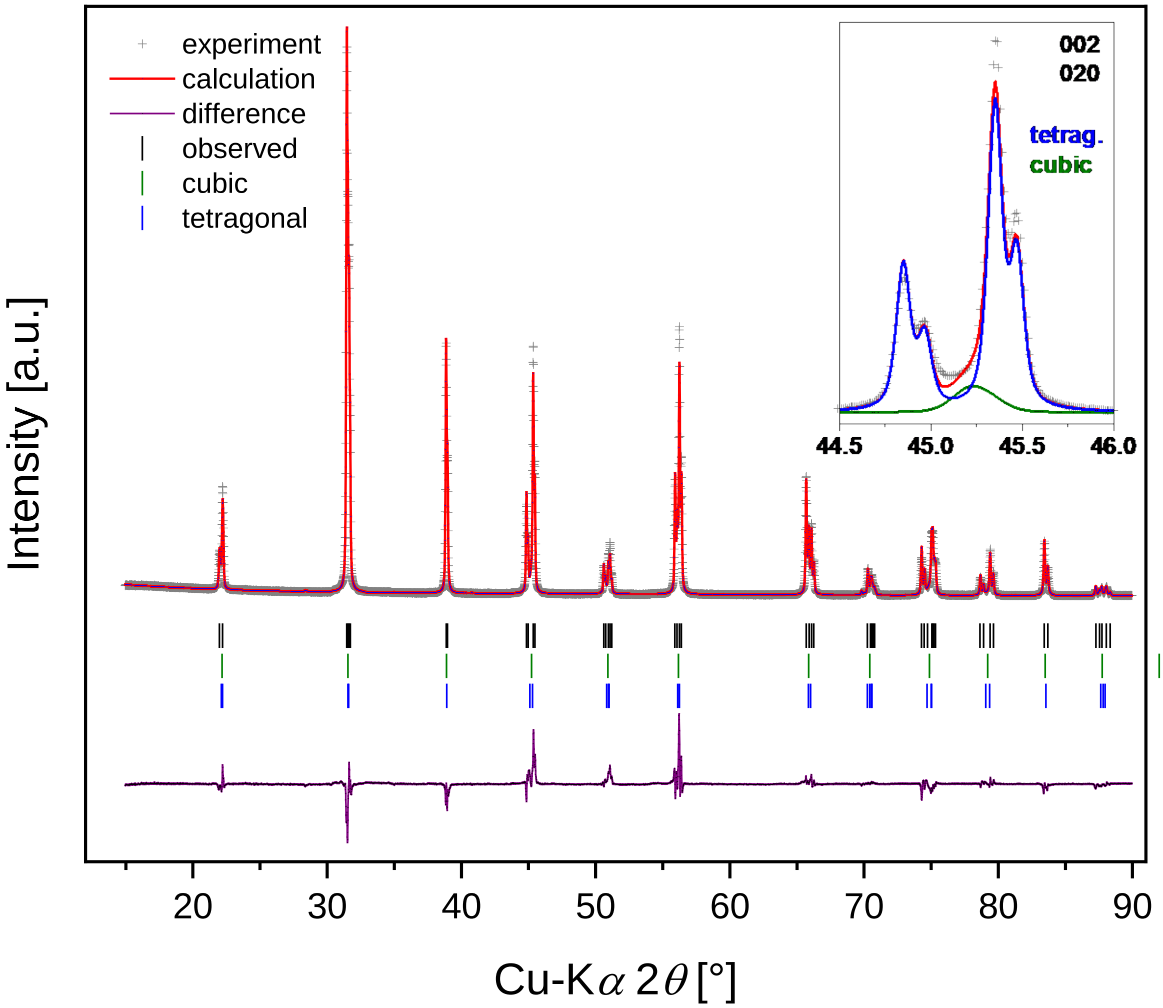


Figure S.7. Rietveld refinement results of unpoled $BaTiO_3$ powder with 500 nm nominal particle diameter (BT500). Inset shows composition of 002/020 reflection with respect to cubic and tetragonal fraction.

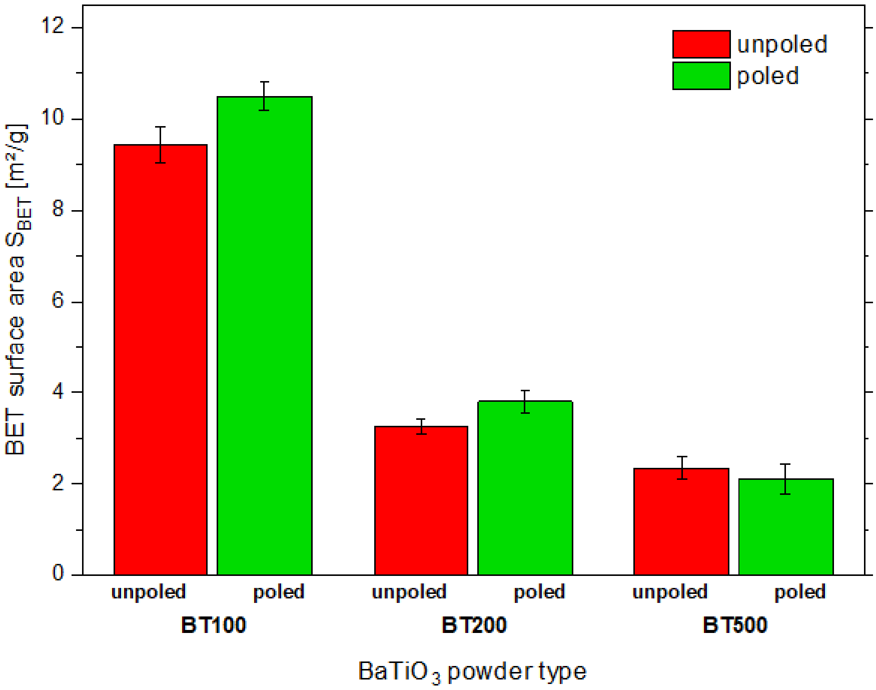


Figure S.8. Comparison of the obtained BET specific surface area S_{BET} for poled and unpoled $BatiO_3$ powders with nominal particle sizes of 100, 200 and 500 nm (BT100, BT200, BT500). BET: Brunauer-Emmett-Teller.