SUPPORTING INFORMATION

Insights into $BaTi_{1-y}Zr_yO_3$ ($0 \leq y \leq 1$) Synthesis under Supercritical Fluid Conditions

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Calculation of crystallite sizes

The Thomson Cox Hastings – pseudo Voigt approximation was used to model the powder diffraction patterns. Thus, the profiles are described by a convolution of Gaussian (normal distribution, G(x)) and Lorentzian (Cauchy distribution, L(x)) components. When normalizing these components (L'(x) and G'(x)) we obtain the information regarding the peaks broadening (FWHM or H'). Each distribution have a different FWHM: H_G and H_L and the shape of the Voigt function depend on the relative importance of both.

$$V(x) = V(x, H_G, H_L)$$

The pseudo Voigt function, pV(x), approximates the Voigt function where H_L and H_G are replaced by the pair (η, H).

$$pV(x) = \eta \mathrm{L}'(\mathrm{x}) + (1 - \eta)\mathrm{G}'(\mathrm{x}) \; with \; 0 \leq \eta \leq 1$$

This equation can then be numerically calculated as:

$$H = \left({H_G}^5 + 2.69269\,.\,{H_G}^4\,.\,H_L + 2.48243\,.\,{H_G}^3.{H_L}^2 + \; 4.47163\,.\,{H_G}^2.{H_L}^3 + 0.07842\,.\,H_G.{H_L}^4 + \; {H_L}^5\right)^{1/5}$$

With

$$H_G = \frac{\sqrt{I_G}}{\cos(\theta)}$$

$$H_L = \frac{Y}{\cos(\theta)}$$

Leading to

$$H = \frac{1}{\cos(\theta)}\left(\sqrt{I_G}^5 + 2.69269\,.\sqrt{I_G}^4\,.Y + 2.48243\,.\sqrt{I_G}^3\,.Y^2 + \; 4.47163\,.\sqrt{I_G}^2\,.Y^3 + 0.07842\,.\sqrt{I_G}\,.Y^4 + \; Y^5\right)^{1/5}$$

Which can be then inserted in the Scherrer equation

$$< D > = \frac{K\,.\,\lambda}{H\,.\cos(\theta)}$$

The uncertainties (σ_D) were calculated with the Equations (1) & (2) where σ_{IG} and σ_Y are the uncertainties on I_G and Y determined through the refinement. In all the results the errors on size calculations were lower than 0.5 nm showing data of high quality:

$$\sigma_D = \left(\frac{0.94\lambda}{H^2}\right) . \sigma_H \quad (1)$$

$$\sigma_H = \frac{\pi}{180} . \sqrt{\frac{Y}{16\, {I_G}^{2/3}} . {\sigma_{I_G}}^2 + \frac{\sigma_{I_G}}{4\, Y} . {\sigma_Y}^2} \quad (2)$$

Figure S1 : Variation of the BTZ mean nanocrystals size, together with their size distributions, determined from TEM pictures with more than 150 nanocrystals for each composition (reprinted from Philippot et al. Ref [2] ***Copyright @ (2015), Elsevier)***

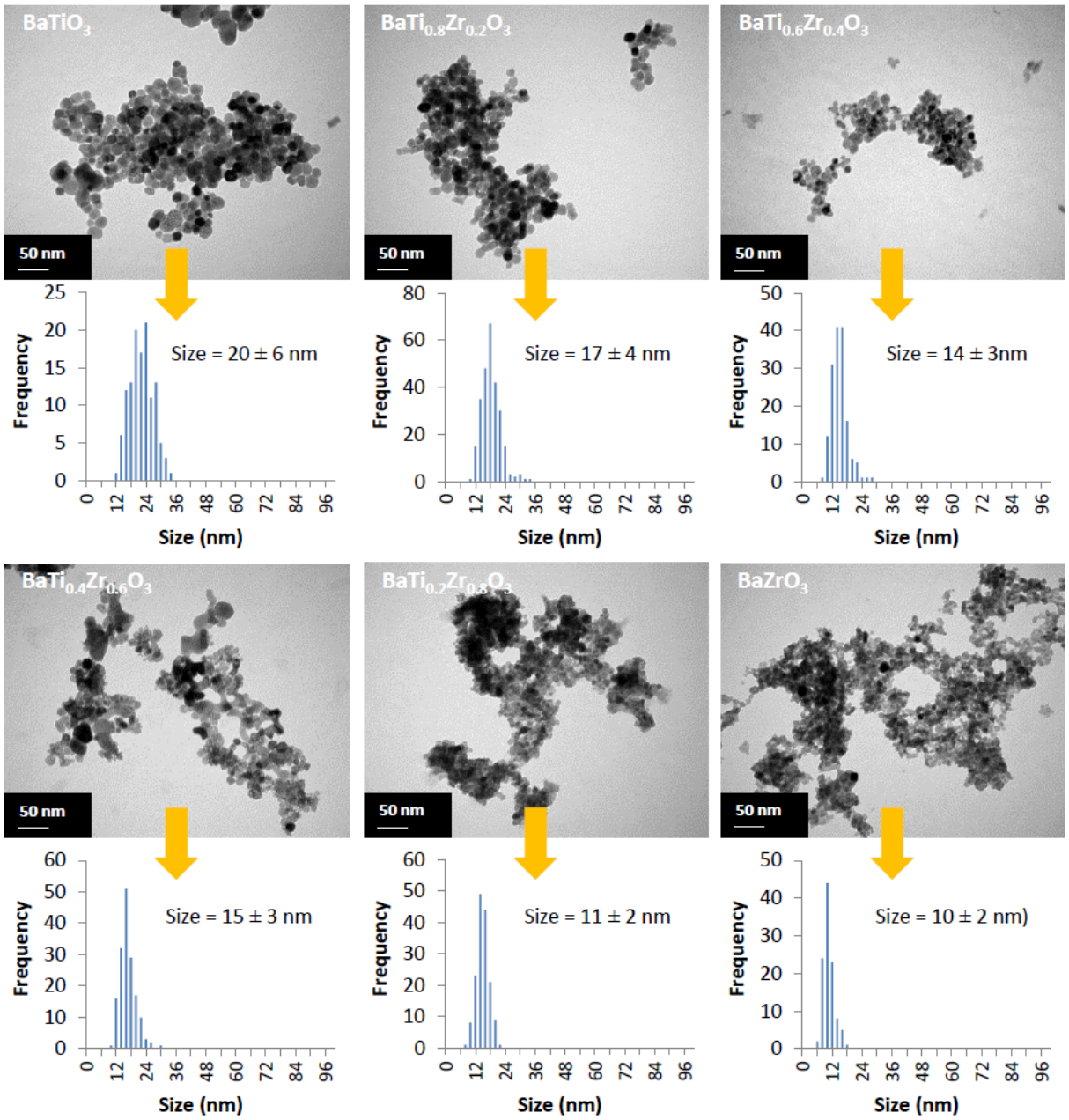


Figure S2 :In situ: Variation of the normalized crystallite size and normalized scale factor with time for $BaTiO_3$, $BaTi_{0.85}Zr_{0.15}O_3$ and $BaTi_{0.70}Zr_{0.30}O_3$ syntheses at 400°C and precursor concentration of 0.2M

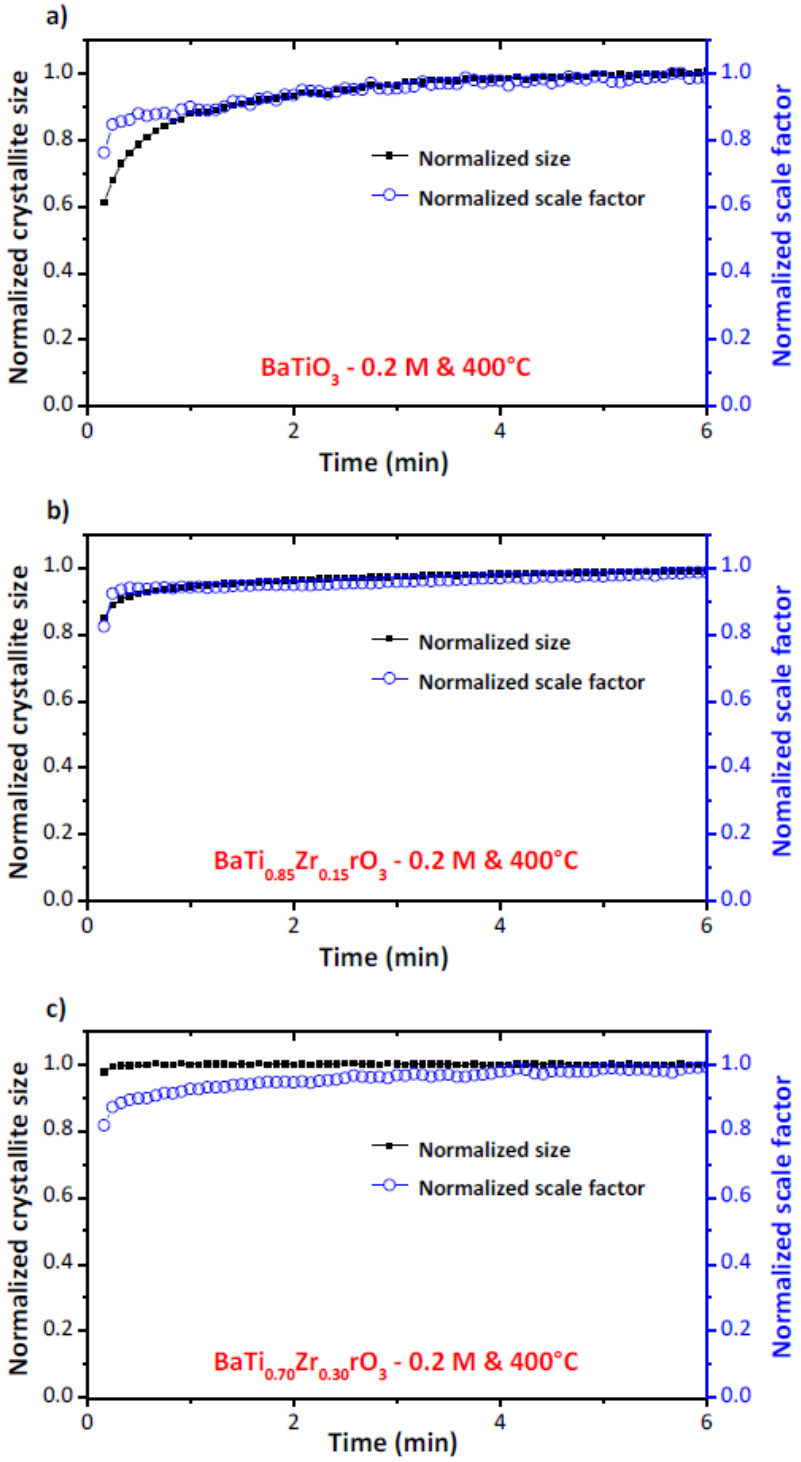
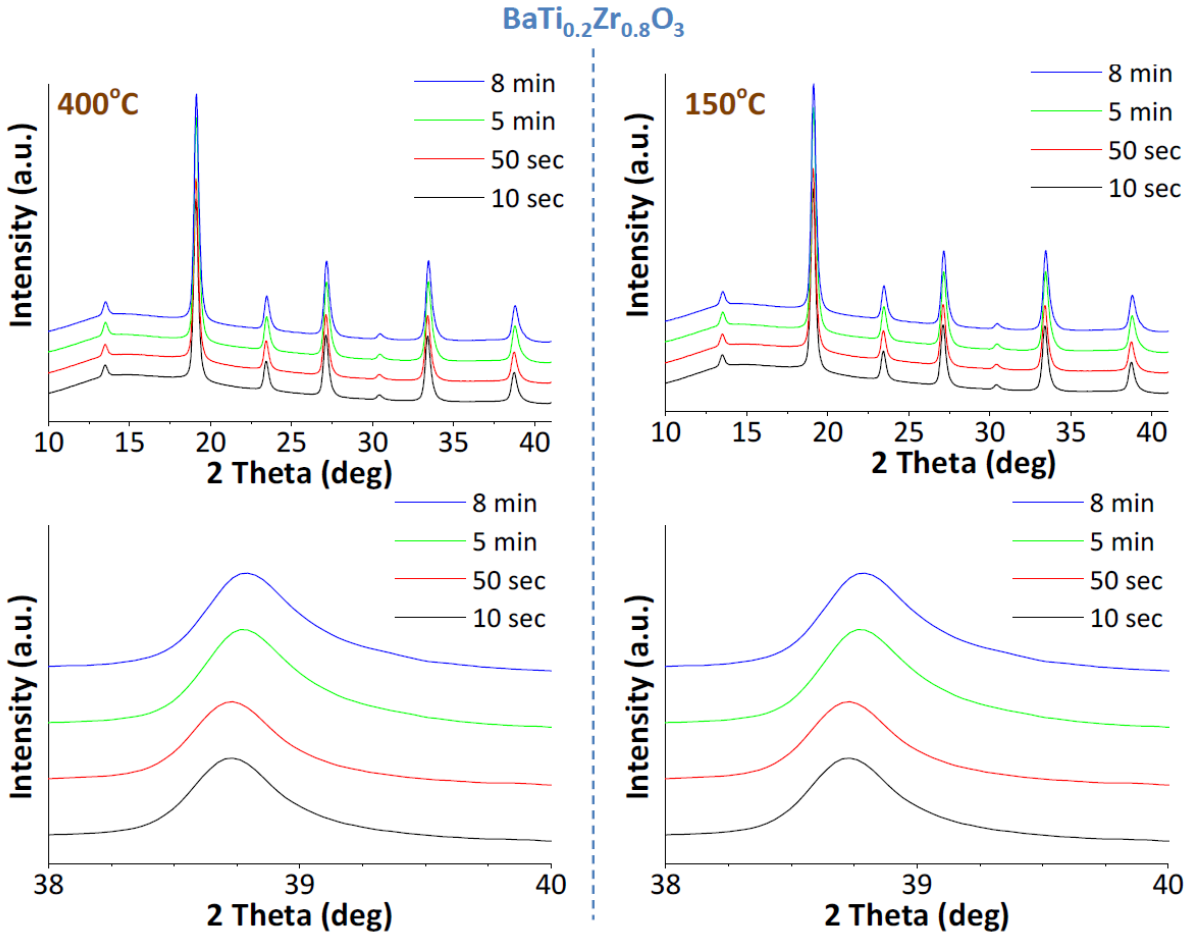
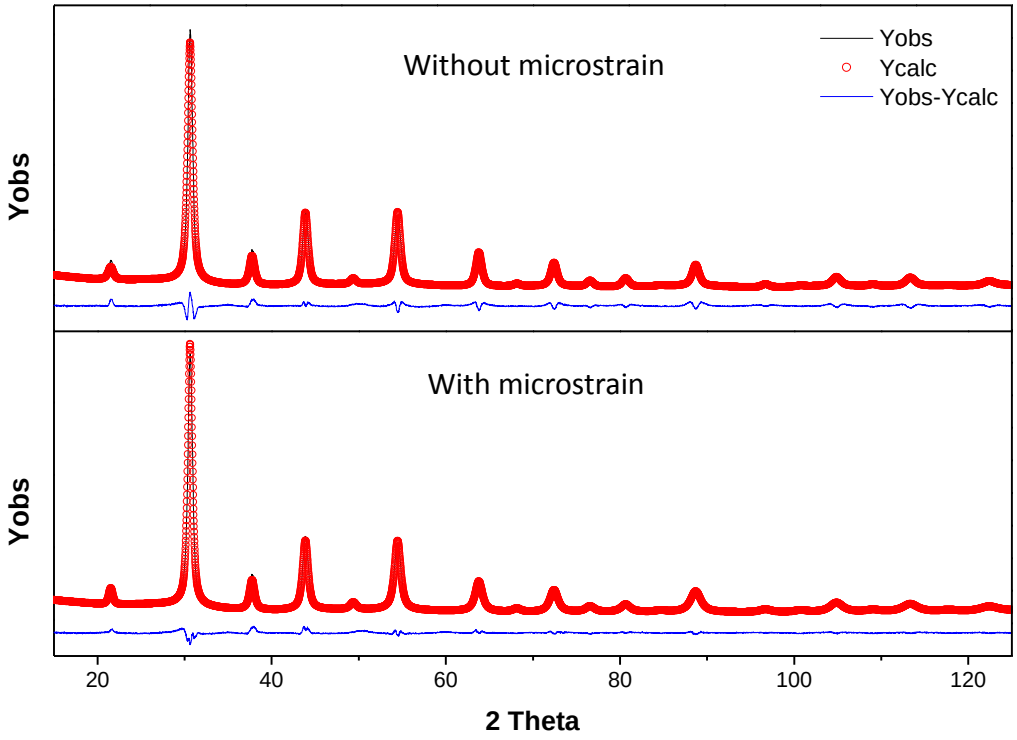


Figure S3 : Variation of the WAXS patterns (λ ≈ 0.99361 Å) during the synthesis of $BaTi_{0.2}Zr_{0.8}O_3$ crystallites at different synthesis temperatures: 400°C and 150°C with a zoom around 39°.



Here the background is higher than for the experiment with y = 0.6, the zirconium amount being higher, the quantity of unreacted precursor, even at 400°C, might be higher due to the lower overall reactivity.

***Figure S4 :Ex situ*: visualization of the microstrain effect on PXRD refinement of the $BaTi_{0.4}Zr_{0.6}O_3$ sample**



This figure presents the visualization of the microstrain effect on the PXRD refinement of the $BaTi_{0.4}Zr_{0.6}O_3$ produced with the flow reactor. There we can see that the modeled pattern including a microstrain parameter presents a better fit to the experimental data than the model without microstrain.

Table T1 : Results of ICP measurements on the BTZ powders produced with the flow reactor

	Ti				Zr				Zr/(Zr+Ti)		
	Concentration		Uncertainty		Concentration		Uncertainty		Calculated		Target
	mg/L	mol/L	mg/L	mol/L	mg/L	mol/L	mg/L	mol/L	Value	Uncertaintty	
$BaTi_{0.85}Zr_{0.15}O_3$	16.45	3.44E-03	0.34	7.10E-05	6.03	6.61E-04	1.19	1.30E-04	**0.16**	0.03	**0.15**
$BaTi_{0.70}Zr_{0.30}O_3$	15.91	3.32E-03	0.34	7.10E-05	14.81	1.62E-03	1.19	1.30E-04	**0.33**	0.02	**0.30**
$BaTi_{0.50}Zr_{0.50}O_3$	10.47	2.19E-03	0.34	7.10E-05	17.63	1.93E-03	1.19	1.30E-04	**0.47**	0.02	**0.50**
$BaTi_{0.40}Zr_{0.60}O_3$	8.78	1.83E-03	0.34	7.10E-05	21.94	2.41E-03	1.19	1.30E-04	**0.57**	0.02	**0.60**
$BaTi_{0.30}Zr_{0.70}O_3$	7.58	1.58E-03	0.34	7.10E-05	29.27	3.21E-03	1.19	1.30E-04	**0.67**	0.02	**0.70**
$BaTi_{0.20}Zr_{0.80}O_3$	4.54	9.48E-04	0.34	7.10E-05	29.2	3.20E-03	1.19	1.30E-04	**0.77**	0.02	**0.80**
$BaTi_{0.10}Zr_{0.90}O_3$	2.52	5.26E-04	0.34	7.10E-05	30.18	3.31E-03	1.19	1.30E-04	**0.86**	0.02	**0.90**

***Table T2 : In situ*: visualization of the 2 phases impact on the refinement in the case of $BaTi_{0.4}Zr_{0.6}O_3$ at 400°C**

	10 seconds			8 minutes		
	2 phases		1 phase	2 phases		1 phase
	Phase 1	Phase 2		Phase 1	Phase 2	
R-Bragg (%)	3.62	3.39	**8.11**	3.43	4.09	**1.60**
B_{iso} Zr/Ti	3.32	3.81	3.02	3.6	3.6	2.95
Unit cell (Å)	4.14	4.19	4.17	4.14	4.16	4.15
Scale (10^{-4})	2.9	4.9	7.9	5.1	7.1	12.3
Y	0.205	0.275	0.271	0.223	0.275	0.247
I_G	0.0819	/	**-0.0202**	0.0163	/	0.0067
X	0.346	1.184	4.59	1.144	1.199	1.998

This table presents a comparison of the refined parameters for the $BaTi_{0.4}Zr_{0.6}O_3$ synthesis at 400°C. At the earliest stage of the synthesis (10 seconds), the PXRD fit shows unphysical negative values making it unrealistic, which is not the case for the 2 phases model. It is interesting to note that the R-Bragg factor is also high for the 1 phase case compare to the 2 phases one. After 8 minutes, both model are realistic but, the single phase one now presents even a lower R-Bragg factor. This one phase model is the one used to refine PXRD samples produced with the flow setup. This observation confirms a similar quality between a 8 minutes batch synthesis with a 50 seconds residence time flow one, both being performed at 400°C.

References

[1] G. Philippot, K. M. Ø. Jensen, M. Christensen, C. Elissalde, M. Maglione, B. B. Iversen, and C. Aymonier, "Coupling in situ synchrotron radiation with ex situ spectroscopy characterizations to study the formation of Ba1−xSrxTiO3 nanoparticles in supercritical fluids," *J. Supercrit. Fluids*, vol. 87, pp. 111–117, Mar. 2014.

[2] G. Philippot, M. Albino, U.-C. Chung, M. Josse, C. Elissalde, M. Maglione, and C. Aymonier, "Continuous BaTi1−yZryO3 (0≤y≤1) nanocrystals synthesis in supercritical fluids for nanostructured lead-free ferroelectric ceramics," *Mater. Des.*, vol. 86, pp. 354–360, 2015.