Self-assembly of one-pot synthesized $Ce_xZr_{1-x}O_2$-$BaO{\cdot}nAl_2O_3$ nanocomposites promoted by site-selective doping of alumina with barium

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SUPPLEMENTARY INFORMATION

Table S1. Textural properties and phase composition of the nanocomposites after calcination at various temperatures.

Sample	Calcination Temperature	BET Surface Area	Al_2O_3 Phases			BHA	Particle size $Ce_{0.2}Zr_{0.8}O_2$
			γ	θ	α		
	[K]	[m^2g^{-1}]	weight %				[nm]
CZ20(30)-BDA	973	264	100				
	1373	99	67	33			11
	1473	19		48	5	47	23
CZ20(13)-BDA	973	280	100				
	1373	118	85	15			10
	1473	72	38	37	8	17	15
CZ20(35)-Al_2O_3 [a]	773	198	100				
	1373	43		100			16
CZ20(13)-Al_2O_3 [a]	773	213	100				
	1373	68		100			14

[a] Conventional CeO2-ZrO2-Al2O3 nanocomposite from a previous study.[1]

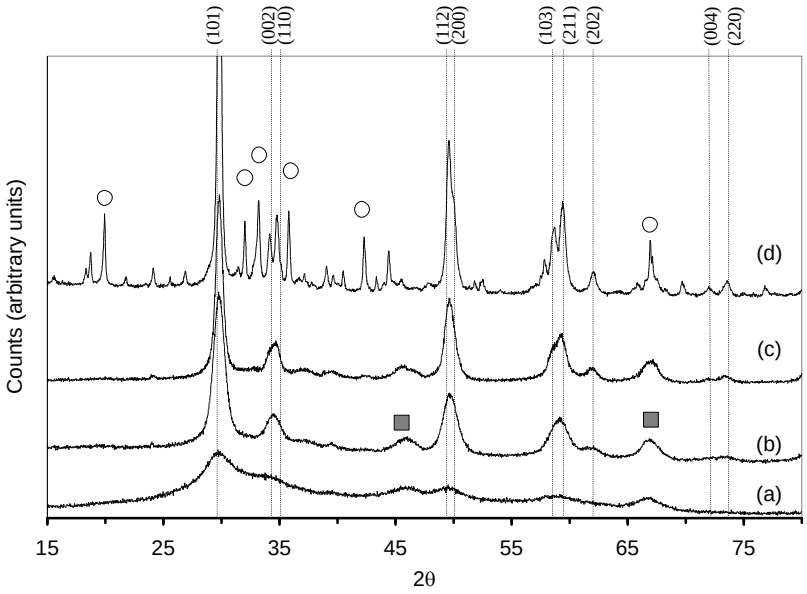

Figure S1. XRD patterns of CZ20(30)-BDA, calcined at (a) 973, (b) 1273, (c) 1373 and (d) 1473 K. ○, BHA; ■, γ-Al_2O_3. Dashed lines represent the reflections due to tetragonal $Ce_{0.2}Zr_{0.8}O_2$.

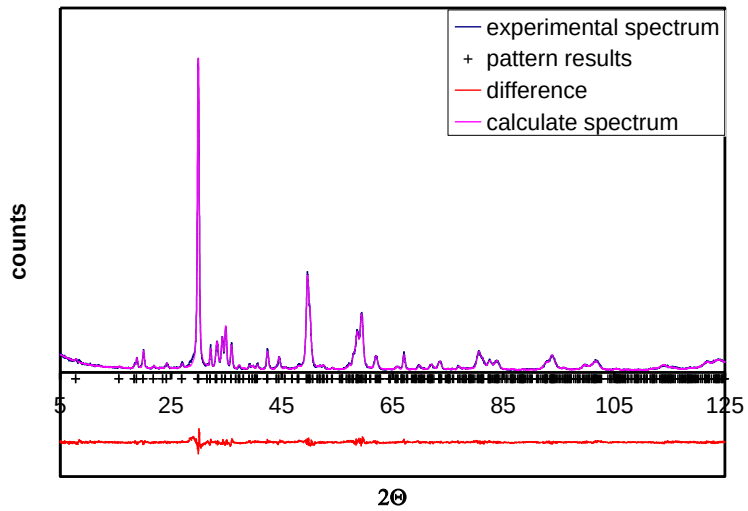

Figure S2. Rietveld structural refinement of the $Ce_{0.2}Zr_{0.8}O_2$(50wt%)-BaO · $5.25Al_2O_3$ calcined at 1473 K. The powder patterns were collected in step scanning mode. The step size used was 0.02 ° 2θ and the counting time was 10 sec/step. The patterns were measured in the range 5-125° 2θ. The refinement was performed with Rietveld method. The general structure analysis system (RIETAN) was used.

Table S2. Results of Rietveld Structural Refinement of XRD patterns of $Ce_{0.2}Zr_{0.8}O_2$(50wt%)-BaO·5.25 Al_2O_3 calcined at 1473 K.

sample	$Ce_{0.2}Zr_{0.8}O_2$(50wt%)-~~BaO~~ BaO·5.25 Al_2O_3
Rwp	10
Phase composition	$Ce_{0.2}Zr_{0.8}O_2$ (TZ) + Ba-$\beta_I\beta_{II}$-Al_2O_3
Nominal TZ(%wt)	50
Calculated TZ (%wt)	49
$Ce_{0.2}Zr_{0.8}O_2$	
Space Group	$P4_2/nmc$
Cell Parameter	$a = b$ = 3.6492(1) Å [a]
	c = 5.2534(2) Å
Ba-$\beta_I\beta_{II}$-Al_2O_3	
Space Group	$P6_3/mmc$
Cell Parameters	$a = b$ = 5.5889(6) Å
	c = 22.744(2) Å
Nominal composition	$Ba_{0.96}Al_{10.83}O_{17.21}$
Calculated composition	$Ba_{0.79}Al_{10.97}O_{17.23}$
Crystallite shape factor	1.0
Calculated ratio β_I/β_{II}	9.8 [b]

[a] Based on the Vegard law, the composition of the solid solution corresponds to $Ce_{0.2}Zr_{0.8}O_2$

[b] nominal value = 1.0

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Table S3. XANES characterisation of the ~~$Ce_{0.2}Zr_{0.8}O_2$CZ20(yy)~~-Al_2O_3 and ~~$Ce_{0.2}Zr_{0.8}O_2$CZ20(yy)-BaO·11.5Al_2O_3BDA~~ nanocomposites: effect of thermal and redox ageing on the fraction of reduced cerium. Results are obtained by linear combination of standard compounds spectra: Ce(III)($CeAlO_3$) and Ce(IV)($Ce_{0.2}Zr_{0.8}O_2$).

Sample	Calcination Temperature	$Ce^{3+}/(Ce^{3+}+Ce^{4+})$		
	[K]	mole fraction		
		Redox Ageing Treatment		
		Not Aged	HTR-LTO	HTR-LTO-HTO
CZ20(30)-BDA	973	0.00		
	1373	0.01		
CZ20(13)-BDA	973	0.00	0.68	0.35
	1373	0.03	0.29	0.14
CZ20(13)/Al_2O_3 – IW	773	0.00	0.52	
	1373	0.29	0.48	

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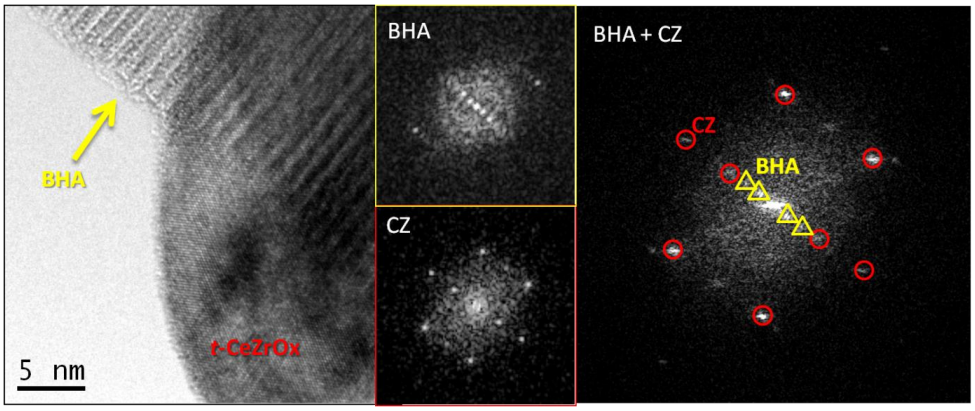

Figure S3. Interaction between the BHA phase and the mixed oxide phase: Consistently the (0001) reflections of the BHA are perfectly aligned with the (-11-2) reflections of the tetragonal Ce-Zr phase. (Left) HREM image for the sample after calcination at 1473 K. (Centre) Digital Diffraction Patterns from both the Barium Hexaaluminate (BHA) area and the tetragonal Ce-Zr nano-crystal. (Right) DDP obtained from the imaged area (BHA+CZ nanocrystal) in which the (0001) reflections -triangles - of the BHA are perfectly aligned with the (-11-2) reflections – circles - of the tetragonal Ce-Zr phase.

[1] R. Di Monte, P. Fornasiero, S. Desinan, J. Kaspar, J. M. Gatica, J. J. Calvino, E. Fonda, *Chem Mater* **2004**, *16*, 4273.