Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

$p(O_2)$-T STABILITY DOMAIN OF CUBIC PEROVSKITE $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$

Aleksey A. Yaremchenko,*[a] Mikhail V. Patrakeev,[b] Eugene N. Naumovich,[c] Dmitry D. Khalyavin [d]

[a] *CICECO – Aveiro Institute of Materials, Department of Materials and Ceramic Engineering, University of Aveiro, 3810-193 Aveiro, Portugal*

[b] *Institute of Solid State Chemistry, UB RAS, 91 Pervomayskaya Str., 620990 Yekaterinburg, Russia*

[c] *Department of High Temperature Electrochemical Processes, Institute of Power Engineering - Research Institute, Augustówka 36, 02-981, Warsaw, Poland*

[d] *ISIS Facility, Rutherford Appleton Laboratory, Harwell Oxford, Didcot, OX11 0QX, United Kingdom*

** Corresponding author. Fax: +351-234-370204; Tel: +351-234-370235; E-mail: ayaremchenko@ua.pt*

Electronic supplementary information

Table S1

Interatomic potentials used for the simulation of point defects in BSCF

Ion	Buckingham			Ref.
	A, eV	ρ, Å	C, $Å^{-6}$	
Ba^{2+}	931.7	0.3949	-	[s1]
Sr^{2+}	1400.0	0.3500	-	[s1]
Co^{3+}	1329.82	0.3087	-	[s2]
Co^{2+}	696.3	0.3362	-	[s1]
Fe^{3+}	1156.36	0.3299	-	[s1]
O^{2-}	22764.3	0.149	43.0	[s1]

References:

[s1] V. Lewis and C.R.A. Catlow, *J. Phys. C: Solid State Phys.*, 1985, **18**, 1149-1161.

[s2] M. Cherry, M.S. Islam and C.R.A. Catlow, *J. Solid State Chem.*, 1995, **118**, 125-132.

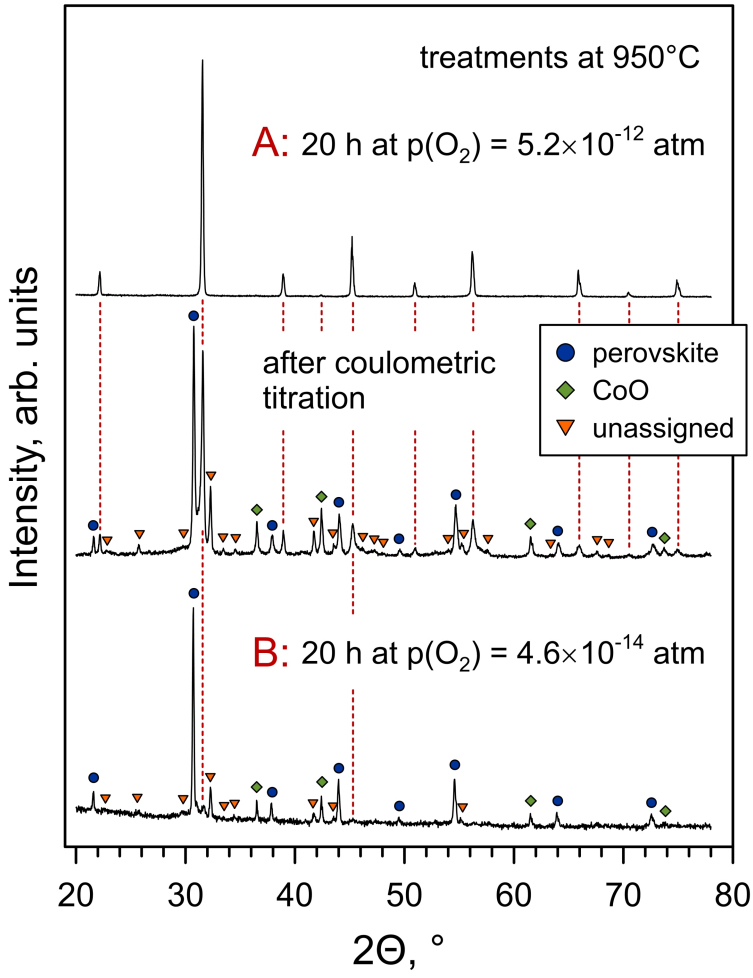

Figure S1. XRD patterns of BSCF samples after low-p(O_2) treatments at 950°C: (center) after stability boundary determination by coulometric titration, and (A and B) after annealing for 20 h at different p(O_2). The conditions A and B correspond to that marked in Fig.1. Vertical dotted lines mark the reflections of cubic perovskite BSCF.

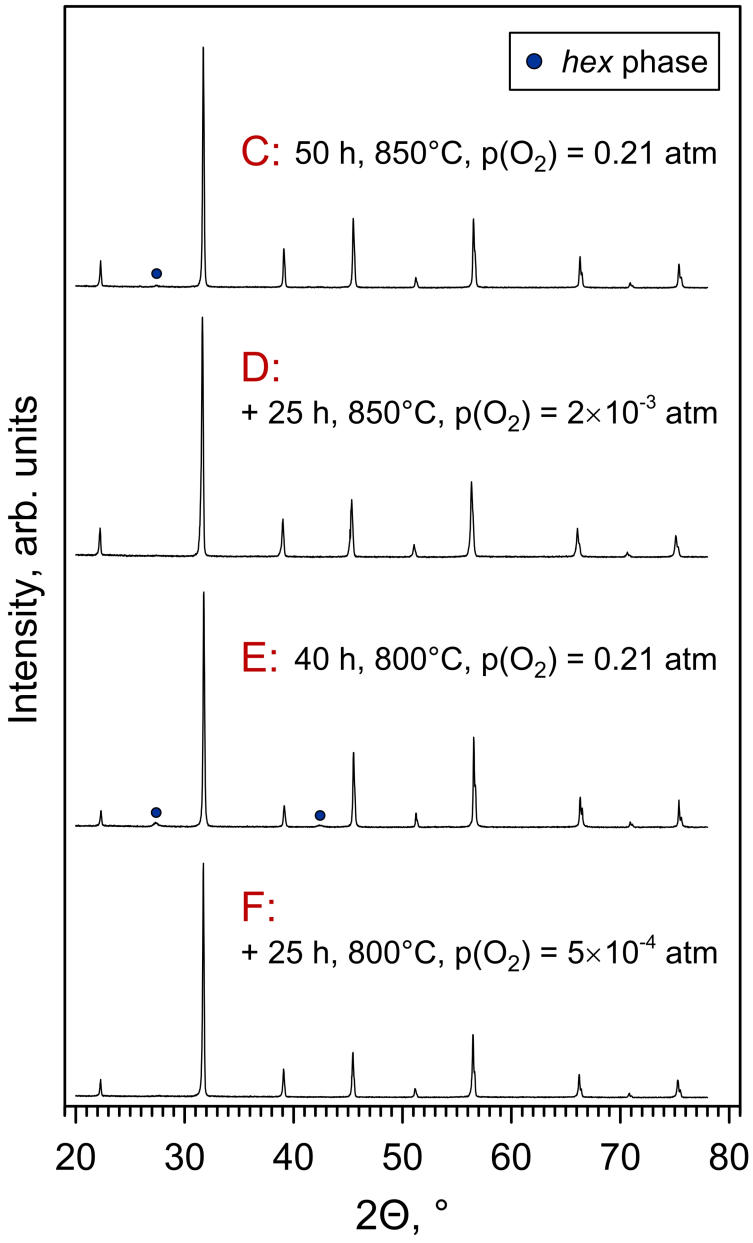

Figure S2. XRD patterns of BSCF samples after annealing in air at 800 or 850°C for 40-50 h (C and E) and then for 25 h at lower $p(O_2)$ at the same temperature (D and F, respectively). The conditions C-F correspond to that marked in Fig.3. Reflections of the hexagonal phase are marked according to Ref.[16].

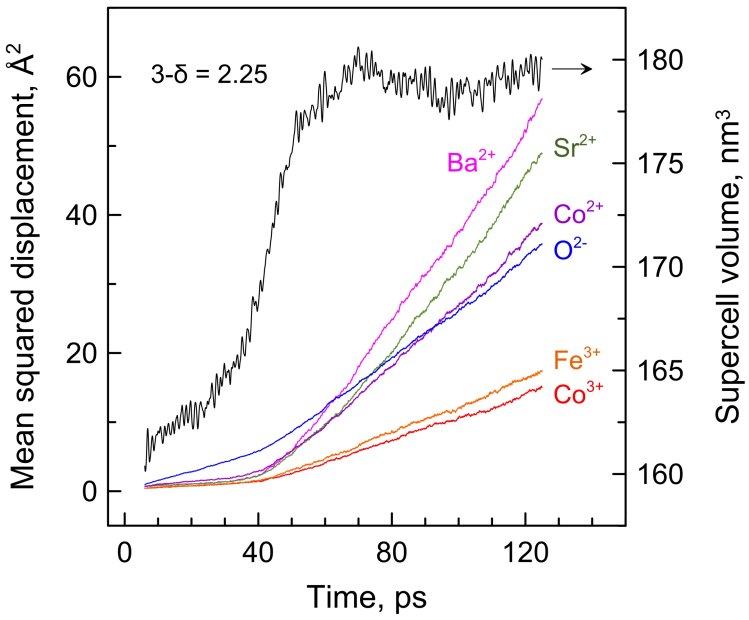

Figure S3. Mean squared displacement of cations and oxygen ions and evolution of the supercell volume during the molecular dynamic simulations of reduced BSCF lattice (3-δ = 2.25): melting process, T = 2200 K.

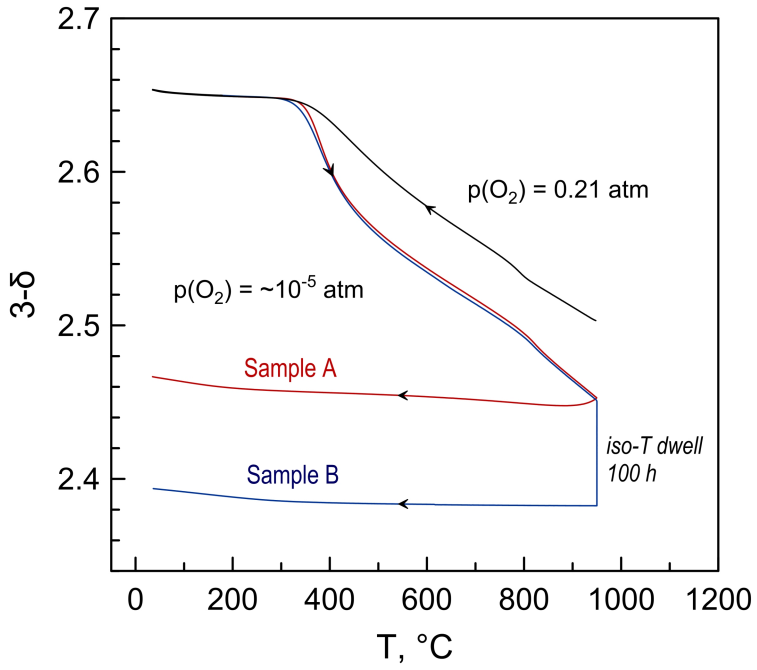

Figure S4. Changes of oxygen nonstoichiometry in BSCF samples on cooling in air and subsequent heating/cooling cycle in inert gas flow. Heating/cooling rate is 2°C/min. After reduction in inert gas, the samples were subjected for the neutron diffraction studies.

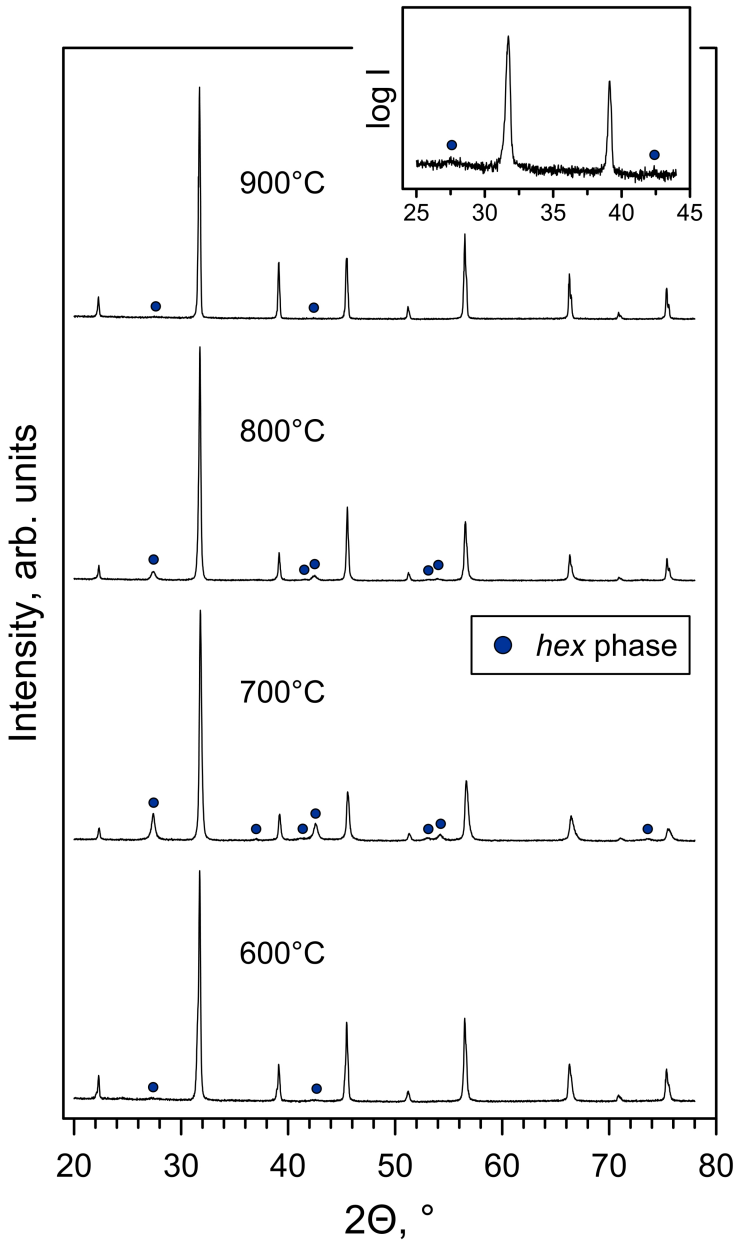

Figure S5. XRD patterns of powdered BSCF samples after annealing in air for 100 h at different temperatures. Reflections of the hexagonal phase are indexed according to Ref.[16]. Inset shows a fragment of the XRD pattern of the sample annealed at 900°C with logarithmic intensity scale.

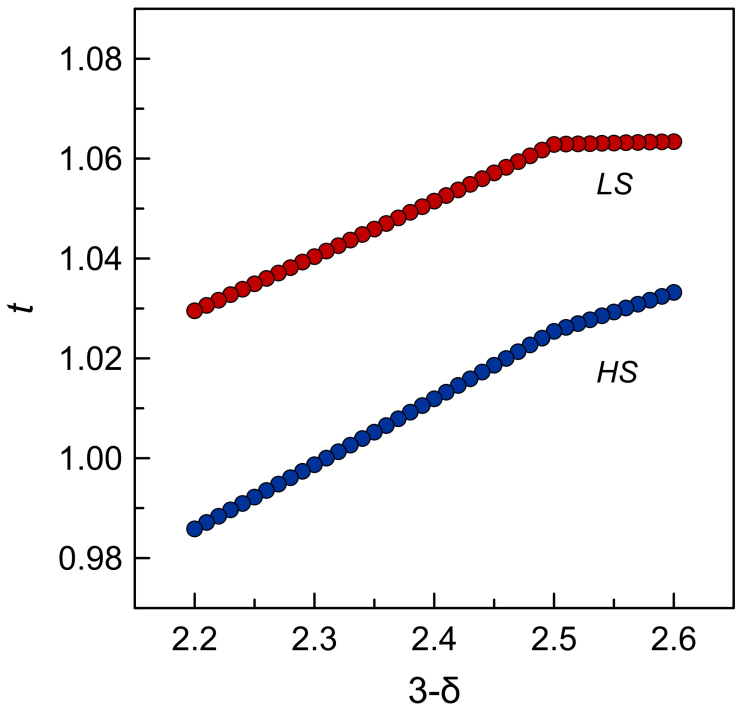

Figure S6. Variations of Goldschmidt tolerance factor $t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$ of BSCF as function of oxygen content in the lattice.

The estimations were done using ionic radii provided by Shannon [s3] and assuming that all iron cations are in 3+ oxidation state when 3-δ ≤ 2.5, oxidation states of iron and cobalt cations are identical when 3-δ > 2.5, and all B-site cations are either in high-spin (*HS*) or low-spin (*LS*) state. The estimations did not take into account the distribution of oxidation and spin state between iron and cobalt cations, possible high-temperature charge disproportionation, changes of the bonds length with temperature, effective size of oxygen vacancies, and variations of coordination number of B-site cations and oxygen anions.

Reference

[s3] R.D. Shannon, *Acta Crystallogr. A*, 1976, **32**, 751-767.