Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Electronic Supplementary Information

Origins of Structural and Electrochemical Influence on Y-doped $BaZrO_3$ Heat-treated with NiO Additive

Donglin Han [a*], Kozo Shinoda [b], Susumu Tsukimoto [c], Hisao Takeuchi [d], Chihiro Hiraiwa [d], Masatoshi Majima [d], Tetsuya Uda [a*]

[a] Department of Materials Science and Engineering, Kyoto University,
Yoshida Honmachi, Sakyo-ku, Kyoto 606-8501, Japan

[b] Institute of Multidisciplinary Research for Advanced Materials, Tohoku University,
Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan

[c] Advanced Institute for Materials Research, Tohoku University,
Katahira 2-1-1, Aoba-ku, Sendai 980-8577, Japan

[d] Sumitomo Electric Industries, Ltd.,
1-1-1, Koyakita, Itami-shi, Hyogo 664-0016, Japan

* Corresponding author: Donglin Han (han.donglin.8n@kyoto-u.ac.jp)
and Tetsuya Uda (materials_process@aqua.mtl.kyoto-u.ac.jp)
TEL: +81-75-753-5445, FAX: +81-75-753-5284

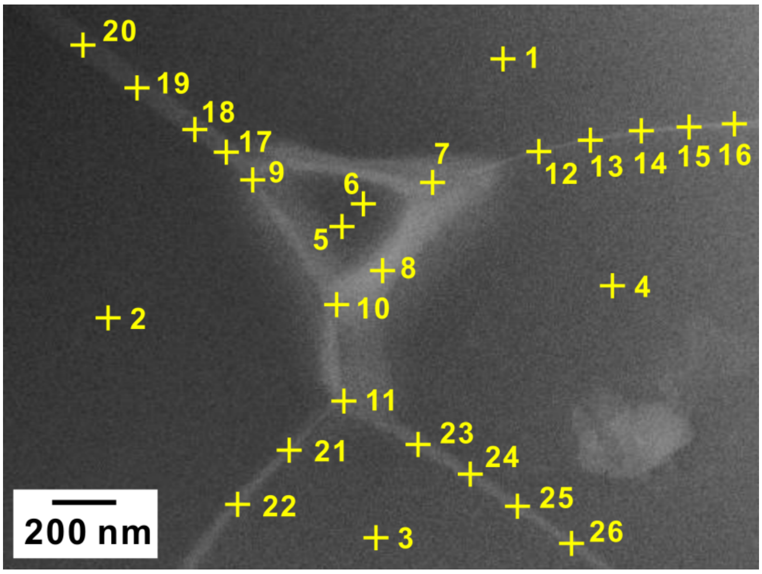

Fig. S1 Positions for STEM-EDS point-analysis on BZY20 – 5 NiO heat-treated at 1600 °C in air for 24h.

Table S1 STEM-EDS point-analysis results on BZY20 – 5 NiO heat-treated at 1600 °C in air for 24h. The numbers are corresponding to the positions marked in Fig. S1.

Position	Number	Cation ratio / at%				Position	Number	Cation ratio / at%			
		Ba	Zr	Y	Ni			Ba	Zr	Y	Ni
Bulk (intra -grain)	1	53.48	40.99	5.13	0.40	Grain boundary	14	47.85	40.07	10.85	1.22
	2	49.03	43.51	7.15	0.31		15	48.88	40.13	9.29	1.69
	3	54.51	34.49	9.95	1.05		16	52.83	36.76	9.37	1.05
	4	55.42	35.32	9.22	0.04		17	52.97	39.07	6.62	1.35
Triple junction	5	0.99	1.88	0.51	96.61		18	52.77	38.84	7.19	1.20
	6	0.86	0.61	0.07	98.46		19	51.68	40.02	7.24	1.06
	7	9.71	7.99	1.75	80.55		20	52.11	40.33	6.34	1.22
	8	6.03	3.84	1.37	88.76		21	54.23	36.55	7.69	1.53
	9	3.09	2.27	0.82	93.82		22	52.39	36.87	9.65	1.09
	10	21.22	15.23	3.95	59.59		23	53.97	39.59	5.20	1.24
	11	35.04	23.79	8.23	32.93		24	53.98	38.15	6.83	1.04
Grain boundary	12	52.14	37.25	8.73	1.88		25	50.23	39.75	8.97	1.05
	13	52.14	37.25	8.73	1.88		26	48.92	43.01	6.90	1.16

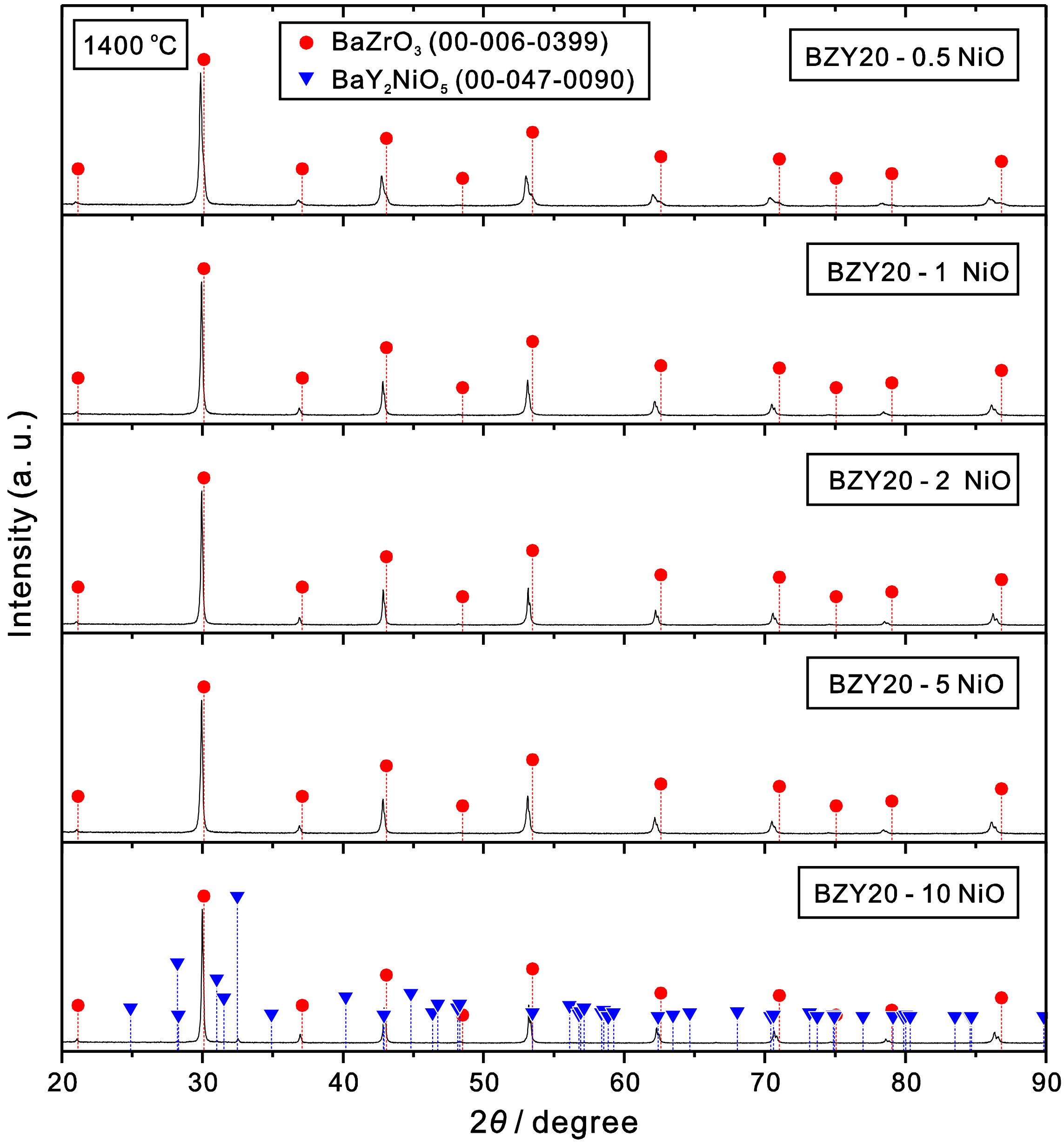

Fig. S2 XRD patterns of BZY20 mixing with various content of NiO. Samples were heat-treated at 1400 °C for 24 h.

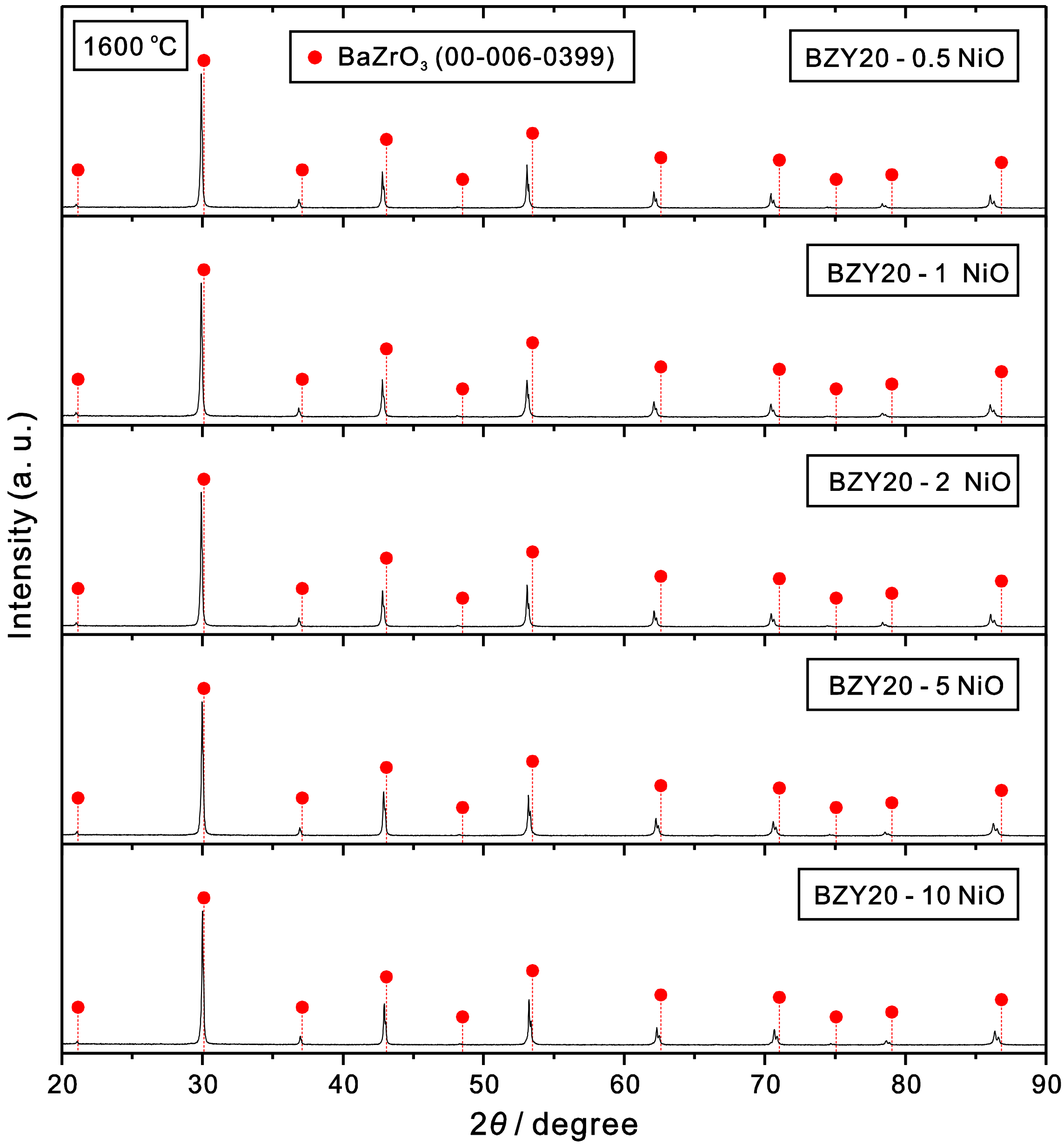

Fig. S3 XRD patterns of BZY20 mixing with various content of NiO. Samples were heat-treated at 1600 °C for 24 h.

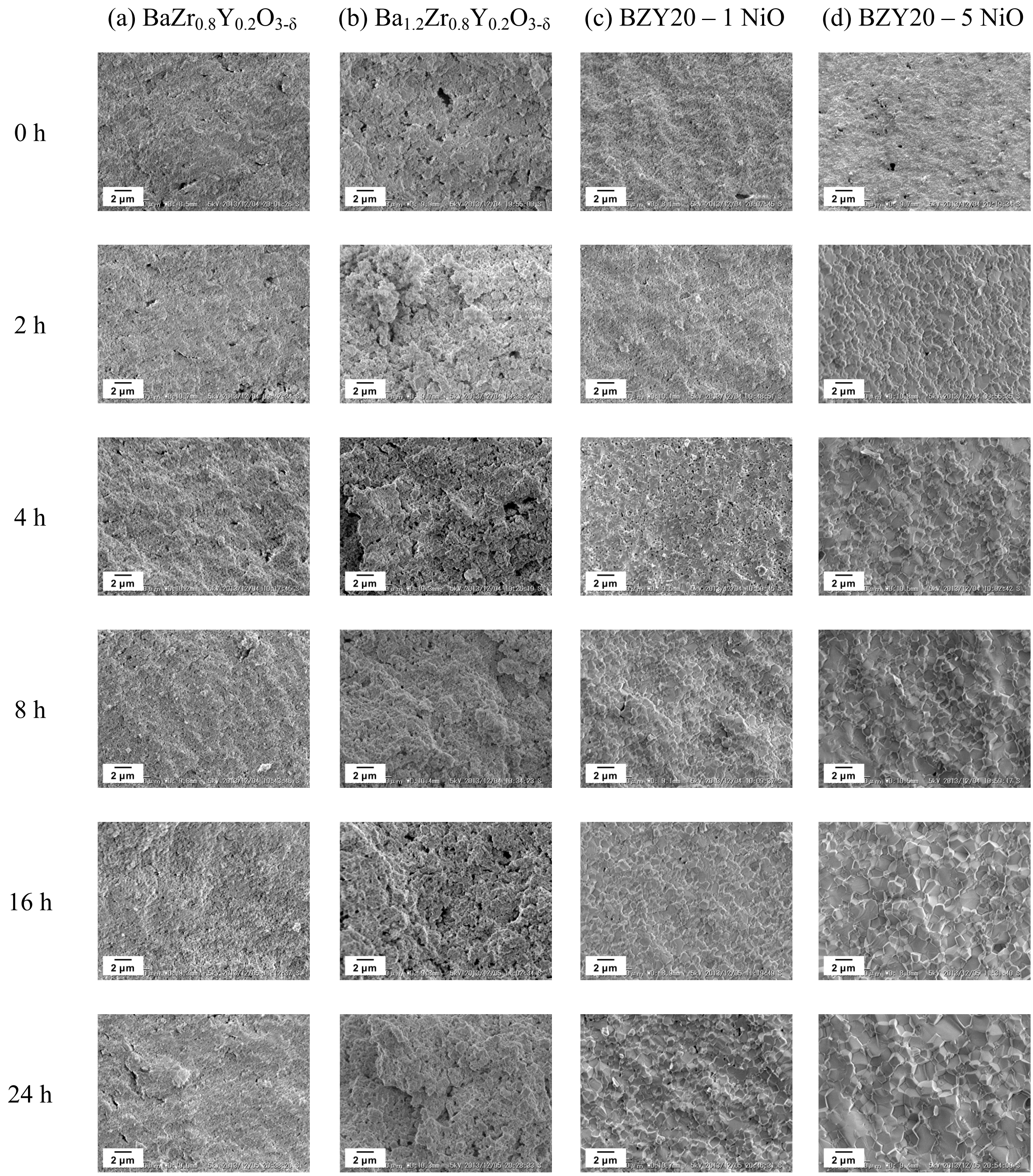

Fig. S4 SEM images of fractured cross-section of (a) BZY20, (b) $Ba_{1.2}Zr_{0.8}Y_{0.2}O_{3-\delta}$, (c) BZY20 – 1 NiO, and (d) BZY20 – 5 NiO, which were heat-treated at 1400 ^{o}C in air at various time, and finally quenched in ambient atmosphere.

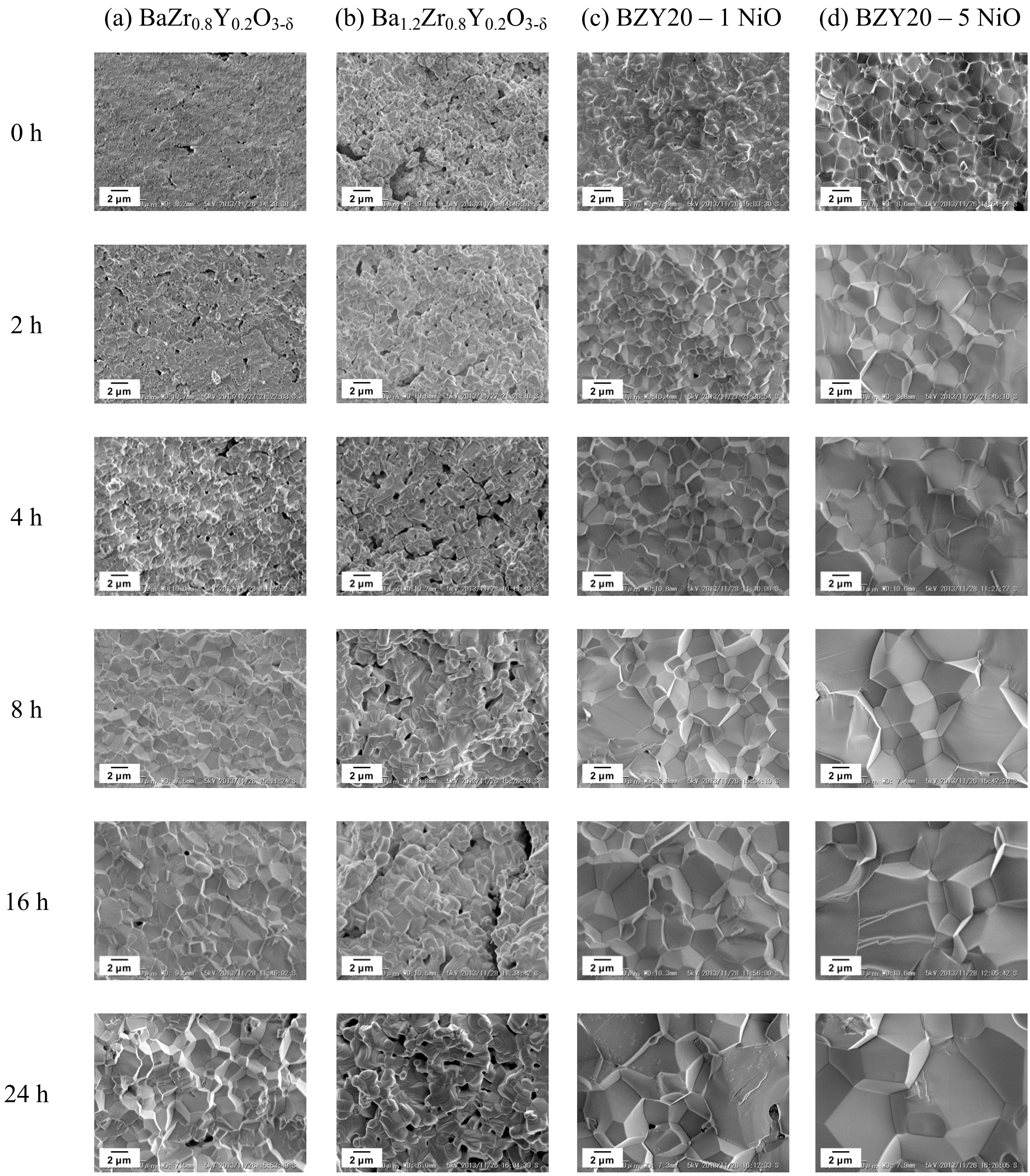

Fig. S5 SEM images of fractured cross-section of (a) BZY20, (b) $Ba_{1.2}Zr_{0.8}Y_{0.2}O_{3-\delta}$, (c) BZY20 – 1 NiO, and (d) BZY20 – 5 NiO, which were heat-treated at 1600 ^{o}C in air at various time, and finally quenched in ambient atmosphere.

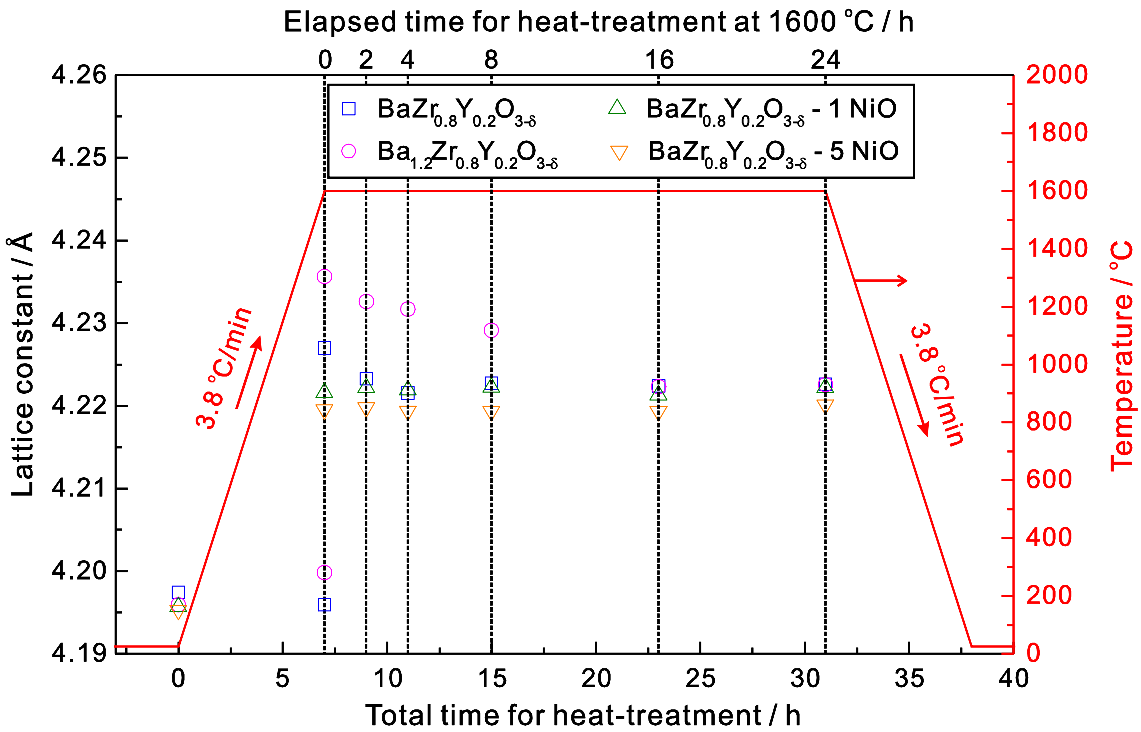

Fig. S6 Lattice constants of the perovskite phases ($Pm\overline{3}m$) in $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ (BZY20), $Ba_{1.2}Zr_{0.8}Y_{0.2}O_{3-\delta}$, BZY20 – 1 NiO, and BZY20 – 5 NiO, which were heat-treated at 1600 °C in air at various time, and finally quenched in ambient atmosphere.

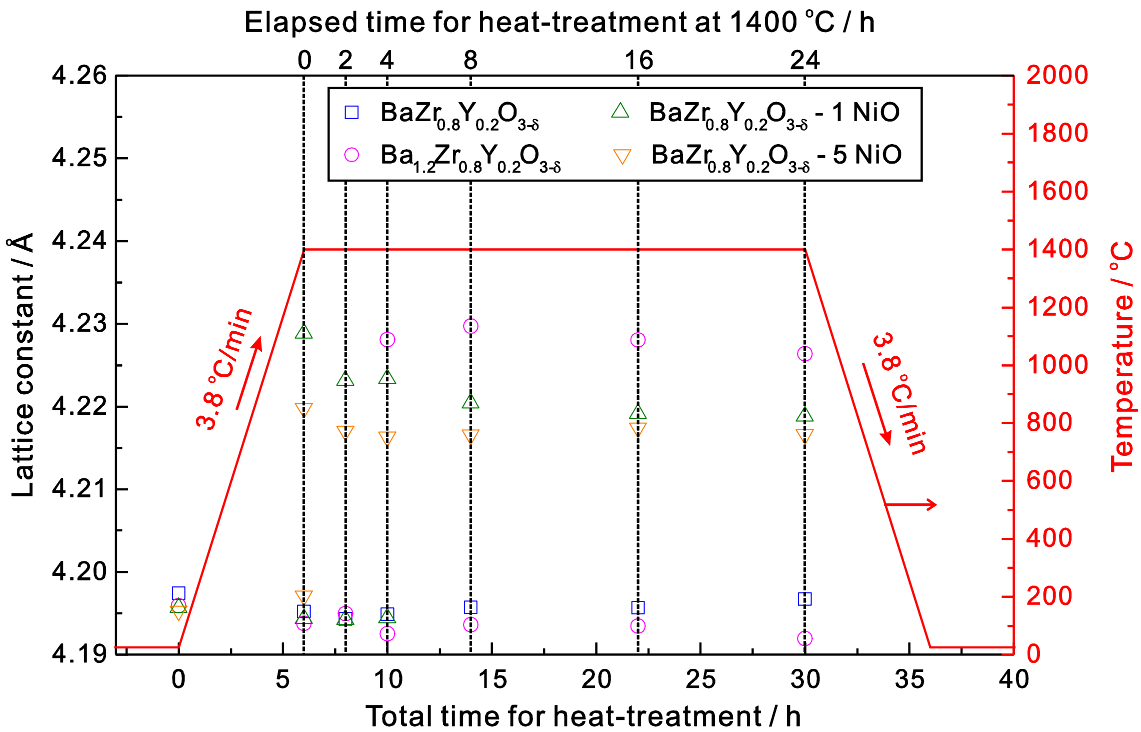

Fig. S7 Lattice constants of the perovskite phases ($Pm\overline{3}m$) in $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ (BZY20), $Ba_{1.2}Zr_{0.8}Y_{0.2}O_{3-\delta}$, BZY20 – 1 NiO, and BZY20 – 5 NiO, which were heat-treated at 1400 °C in air at various time, and finally quenched in ambient atmosphere.

Fitting of EXAFS data of Zr *K*-edge and Y *K*-edge

The structure model used to fit the data on Zr *K*-edge is constructed as follows: (1) Zr - O first shell; (2) Zr – Ba second shell; (3) Zr – Zr/Y third shell; (4) Zr – O2 forth shell; and (5) Zr – Zr/Y fifth shell.

The structure model for fitting the data on Y *K*-edge is constructed as four shells: (1) Y - O first shell; (2) Y – Ba second shell; (3) Y – Zr/Y third shell; and (4) Y – O2 forth shell.

The fitting of the Zr *K*-edge and Y *K*-edge EXAFS data are shown in Fig. S8 and S9, respectively. The fitting of Fourier-transformed Zr and Y *K*-edge EXAFS data of the BZY20 – 1 NiO heat-treated at 1400 °C are given for example in Fig. S10 and S11, respectively. All the fitting results are summarized in Table S2 and S3. The results of BZY20 without NiO addition are in good agreement with the $BaZr_{0.85}Y_{0.15}O_{3-\delta}$ sample studied by Giannici *et al.* (F. Giannici, M. Shirpour, A. Longo, A. Martorana, R. Merkle and J. Maier, *Chem. Mater.* 2011, **23**, 2994.) And there is little difference on the distance between Zr or Y to each shell by introducing small content of NiO into BZY20.

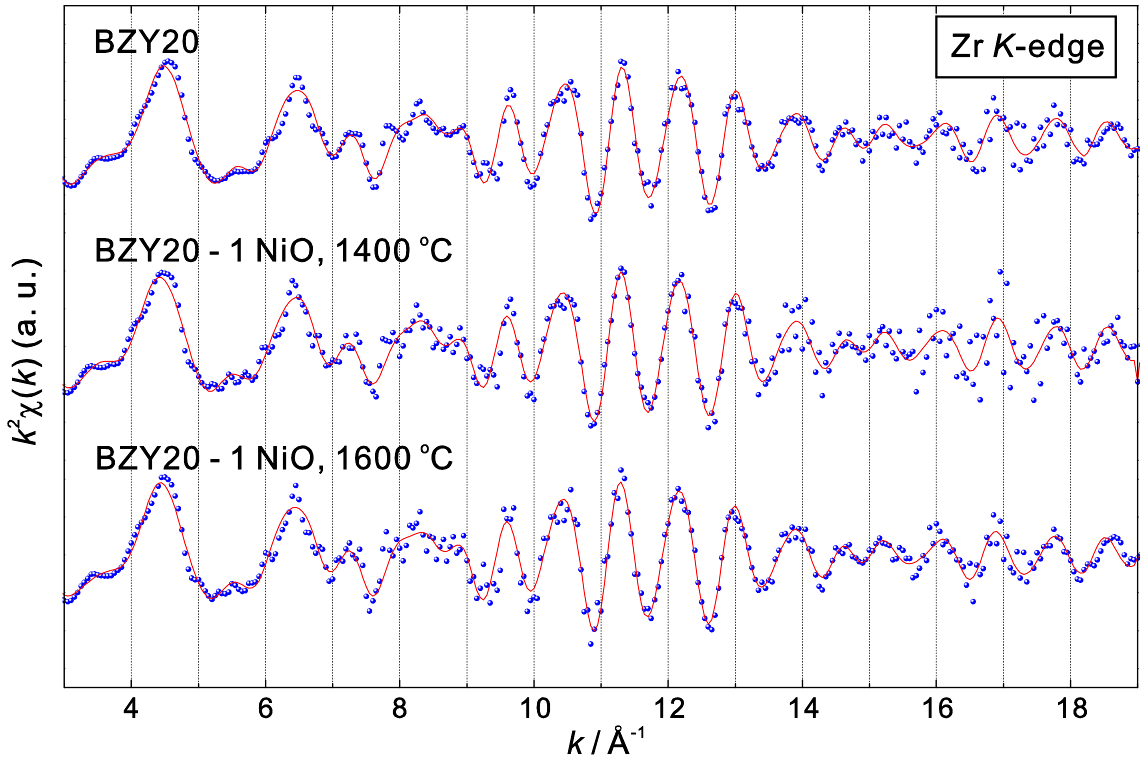

Fig. S8 Zr *K*-edge EXAFS data (circles) and best fit (red line) of BZY20, BZY20 – 1 NiO heat-treated at 1400 °C and 1600 °C in air for 24 h. Data were collected at 8 K in vacuum.

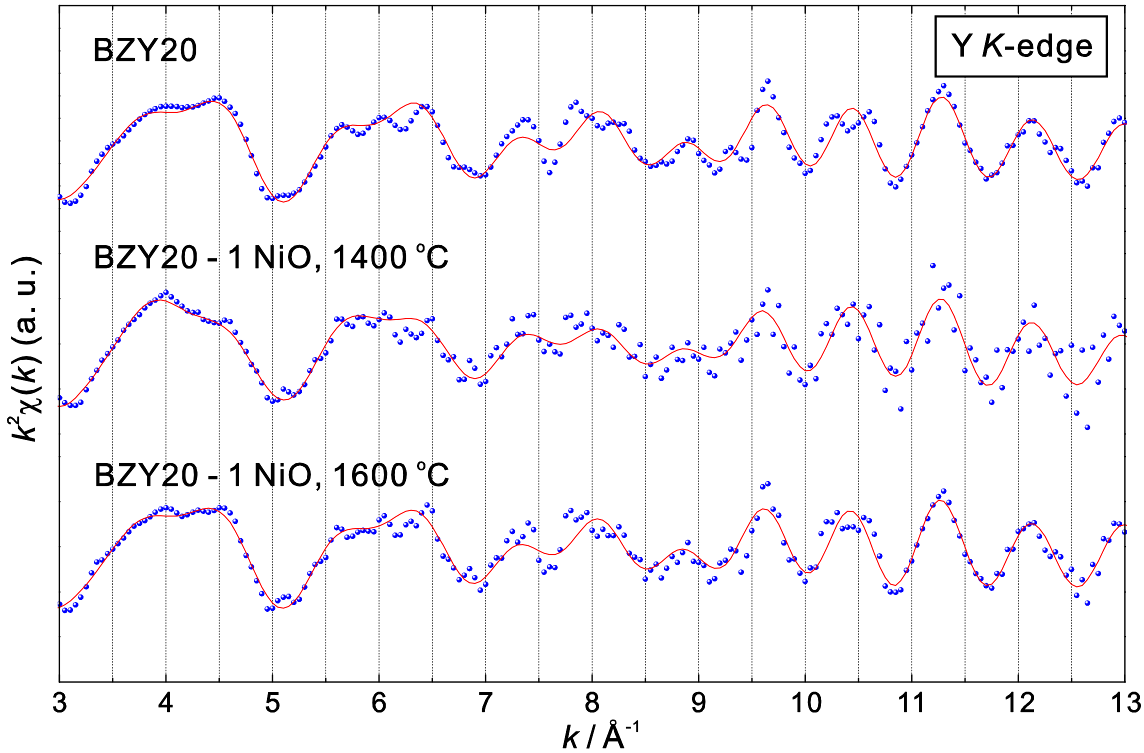

Fig. S9 Y *K*-edge EXAFS data (circles) and best fit (red line) of BZY20, BZY20 – 1 NiO heat-treated at 1400 °C and 1600 °C in air for 24 h. Data were collected at 8 K in vacuum.

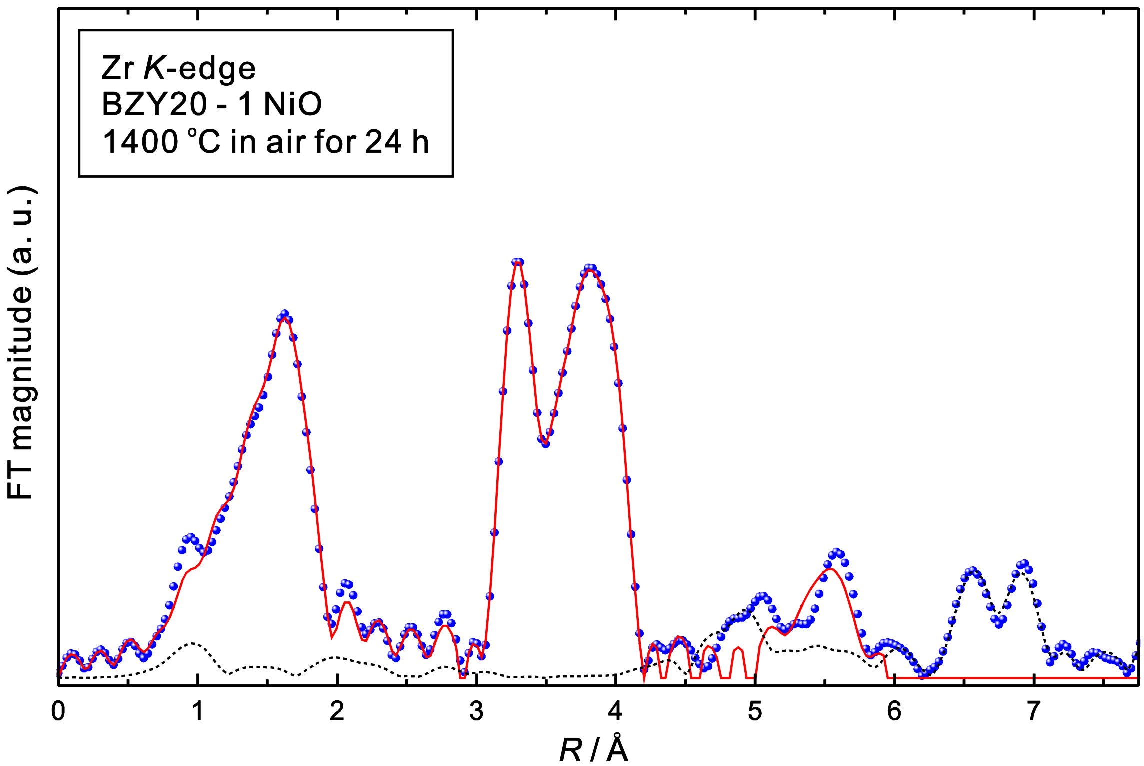

Fig. S10 Fourier-transformed Zr *K*-edge EXAFS data (circles), best fit (solid line), and residual (dash line) of BZY20 – 1 NiO heat-treated at 1400 °C in air for 24 h. Data were collected at 8 K in vacuum.

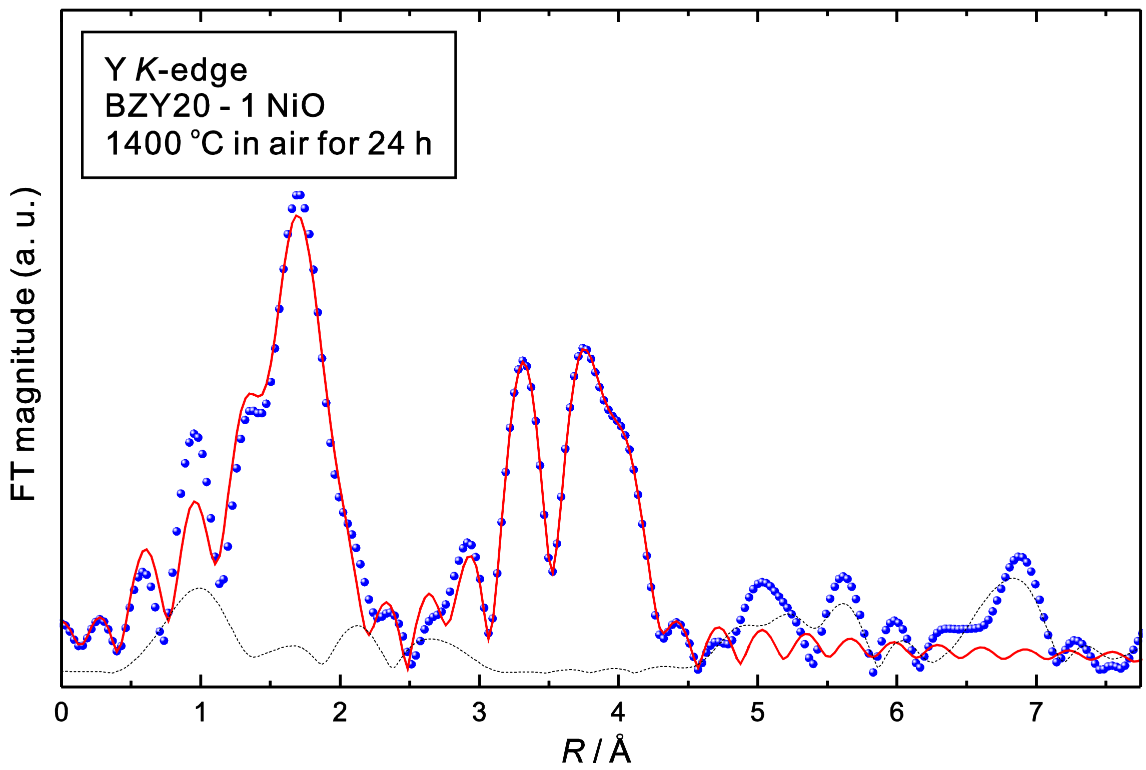

Fig. S11 Fourier-transformed Y *K*-edge EXAFS data (circles), best fit (solid line), and residual (dash line) of BZY20 – 1 NiO heat-treated at 1400 °C in air for 24 h. Data were collected at 8 K in vacuum.

Table S2 EXAFS results for BZY20 and BZY20 – 1 NiO on the Zr-*K* edge. The EXAFS measurements were performed at 8 K in vacuum.

		BZY20	BZY20 – 1 NiO	
Heat-treatment temperature / °C		1600	1400	1600
Zr – O	*R* / Å	2.11	2.11	2.11
	σ^2 / Å^2	0.0053	0.0054	0.0053
Zr – Ba	*R* / Å	3.67	3.65	3.66
	σ^2 / Å^2	0.0041	0.0025	0.0034
Zr – Zr/Y	*R* / Å	4.21	4.21	4.21
	σ^2 / Å^2	0.0016	0.0021	0.0023
Zr – O2	*R* / Å	4.59	4.57	4.63
	σ^2 / Å^2	0.0209	0.0177	0.0190
Zr – Zr/Y2	*R* / Å	5.97	5.94	5.97
	σ^2 / Å^2	0.0035	0.0036	0.0037

Table S3 EXAFS results for BZY20 and BZY20 – 1 NiO on the Y-*K* edge. The EXAFS measurements were performed at 8 K in vacuum.

		BZY20	BZY20 – 1 NiO	
Heat-treatment temperature / °C		1600	1400	1600
Y – O	*R* / Å	2.22	2.25	2.22
	σ^2 / Å^2	0.0067	0.0088	0.0071
Y – Ba	*R* / Å	3.69	3.69	3.69
	σ^2 / Å^2	0.0101	0.0086	0.0099
Y – Zr/Y	*R* / Å	4.25	4.29	4.25
	σ^2 / Å^2	0.0009	0.0053	0.0006
Y – O2	*R* / Å	4.70	4.67	4.70
	σ^2 / Å^2	0.0073	0.0131	0.0069