

Electronic Supplementary Information

Strategy to Improve Phase Compatibility between Proton Conductive BaZr_{0.8}Y_{0.2}O_{3-δ} and Nickel Oxide

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Fig. S1 shows the images of the BaY_2NiO_5 pellet-like samples after heat-treating at 1500 and 1600 °C for various time and finally quenched in ambient atmosphere. The samples were directly placed on Al_2O_3 plate-like crucibles. The XRD patterns of the residue of BaY_2NiO_5 pellet-like samples are shown in **Fig. S2** and **S3**. It can be seen that products containing Al (BaAl_2O_4 and $\text{Ba}_3\text{Y}_2\text{AlO}_{7.5}$) formed. Such results indicate that BaY_2NiO_5 reacted with the Al_2O_3 crucibles. It is therefore not proper to directly place the BaY_2NiO_5 samples on these Al_2O_3 crucibles.

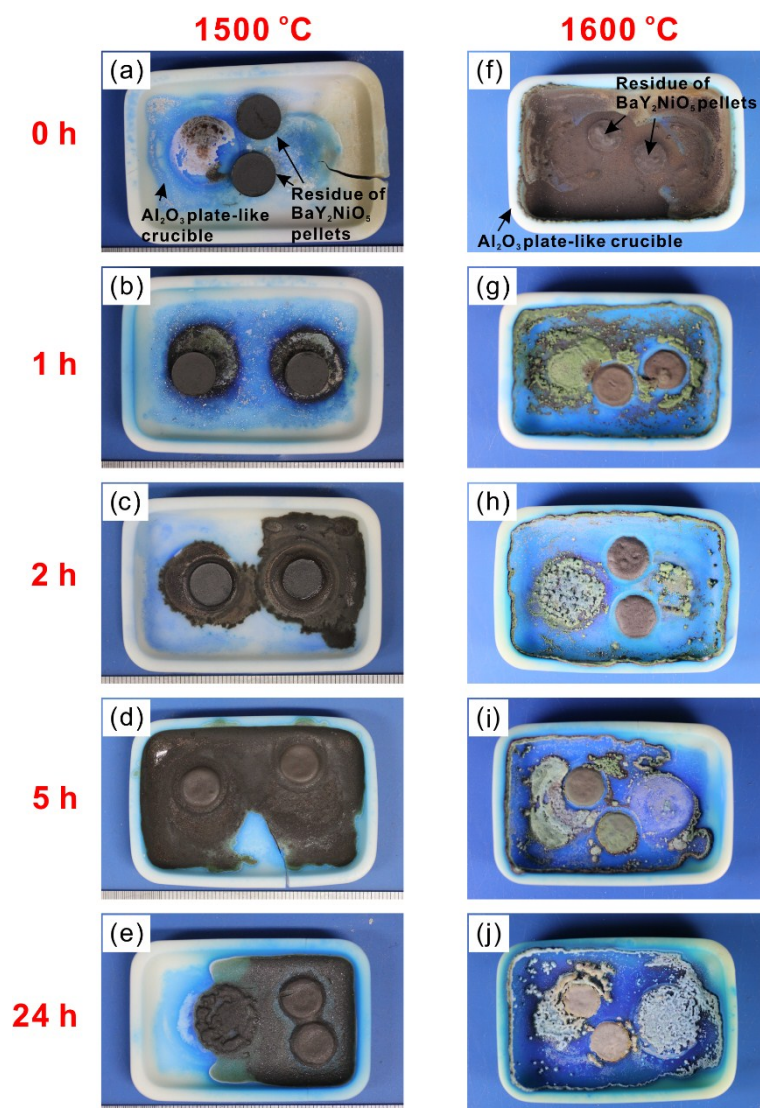


Fig. S1 Optical images of BaY_2NiO_5 pellets heat-treated at 1500 and 1600 °C in ambient atmosphere for various time. The BaY_2NiO_5 pellets were directly placed on Al_2O_3 plate-like crucibles. The heating rates from room temperature to 1000 °C, and 1000 °C to 1500 or 1600 °C were 4.17 and 3.33 °Cmin⁻¹, respectively. All the pellets were finally quenched in ambient atmosphere.

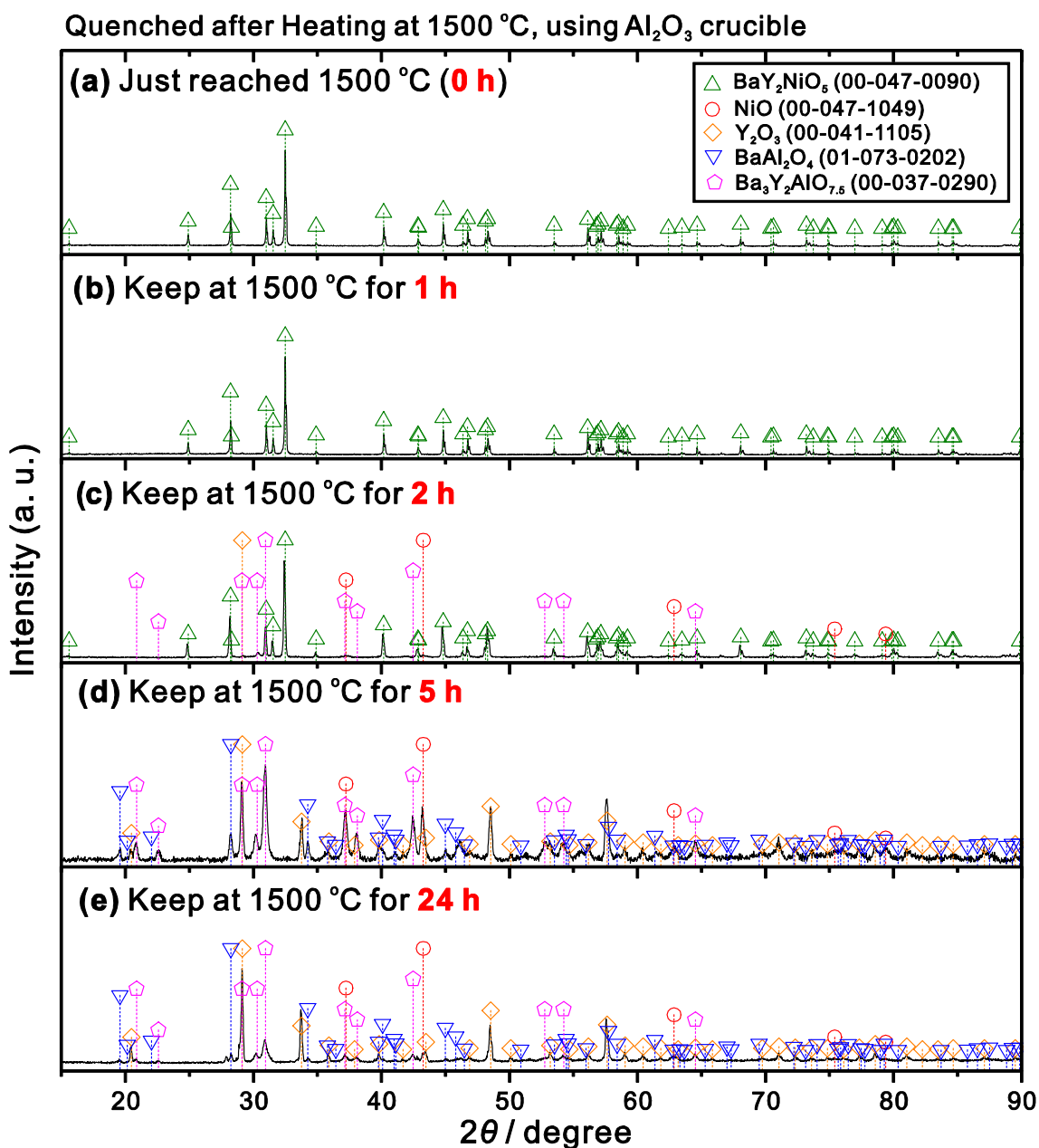


Fig. S2 Powder XRD patterns of the residues of BaY₂NiO₅ pellet-like samples heat-treated at 1500 °C for various time. The pellets were directly placed on Al₂O₃ plate-like crucibles. All the pellets were finally quenched in ambient atmosphere. The heating rates from room temperature to 1000 °C, and 1000 °C to 1500 °C were 4.17 and 3.33 °Cmin⁻¹, respectively. All the pellets were finally quenched in ambient atmosphere.

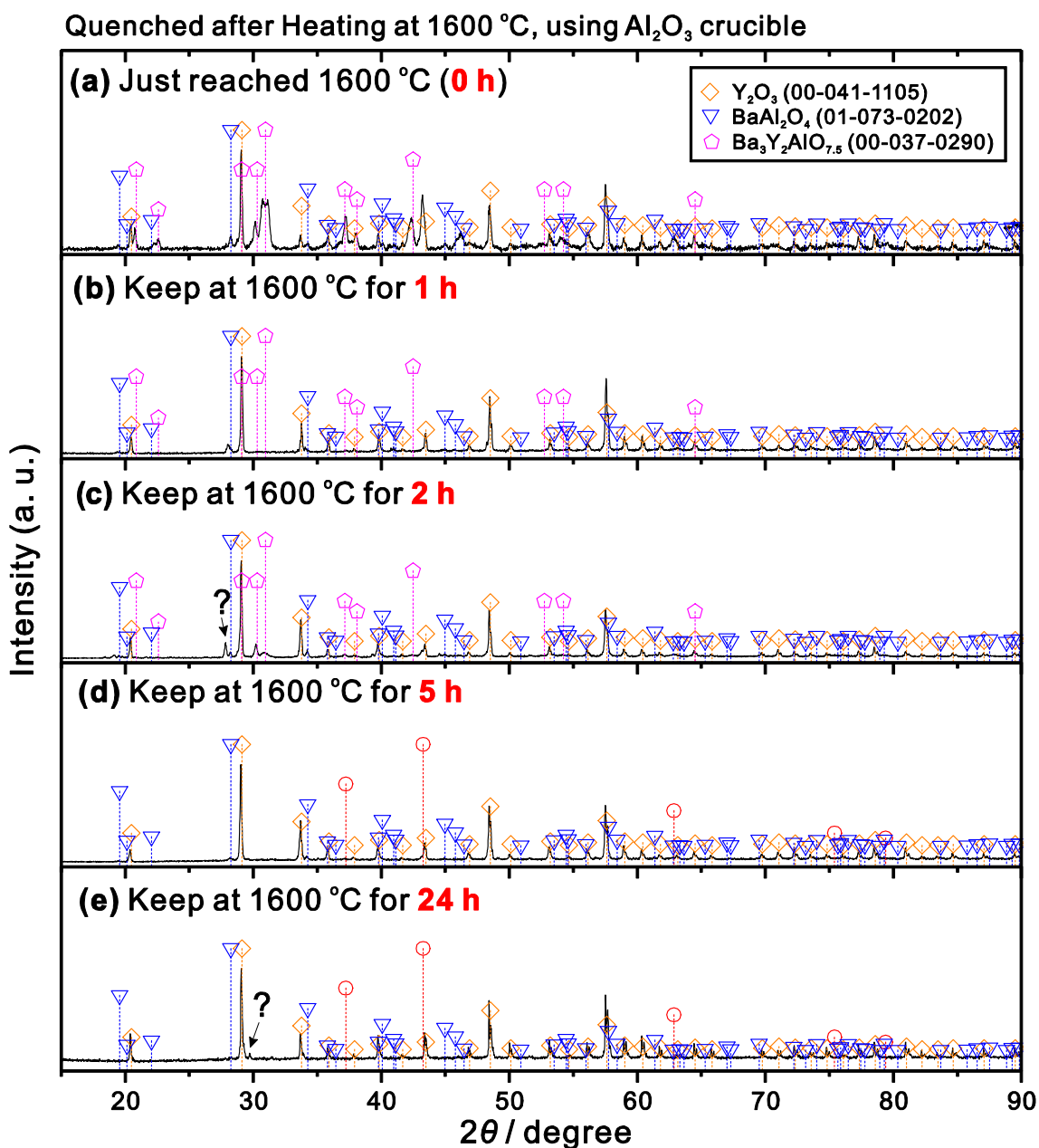


Fig. S3 Powder XRD patterns of the residues of BaY₂NiO₅ pellet-like samples heat-treated at 1600 °C for various time. The pellets were directly placed on Al₂O₃ plate-like crucibles. All the pellets were finally quenched in ambient atmosphere. The heating rates from room temperature to 1000 °C, and 1000 °C to 1600 °C were 4.17 and 3.33 °Cmin⁻¹, respectively. All the pellets were finally quenched in ambient atmosphere.

Table S1 SEM-EDS point analysis results (cation ratio) on the surface of the BaY₂NiO₅ pellet heat-treated at 1600 °C for 0 h (the sample was quenched in ambient atmosphere just after heating up to 1600 °C). The corresponding positions marked with number in **Fig. 6(a)** were examined.

Position	Composition / at%			Possible main phase
	Ba	Y	Ni	
1	23.50	57.04	19.46	BaY ₂ NiO ₅
2	22.35	58.85	18.81	
3	41.23	26.58	32.19	BaNiO ₂ (main) + BaY ₂ NiO ₅ or Y ₂ O ₃
4	54.63	1.96	43.41	BaNiO ₂
5	55.90	2.14	41.95	
6	14.93	70.72	13.34	Y ₂ O ₃ adherent to BaNiO ₂ or BaY ₂ NiO ₅

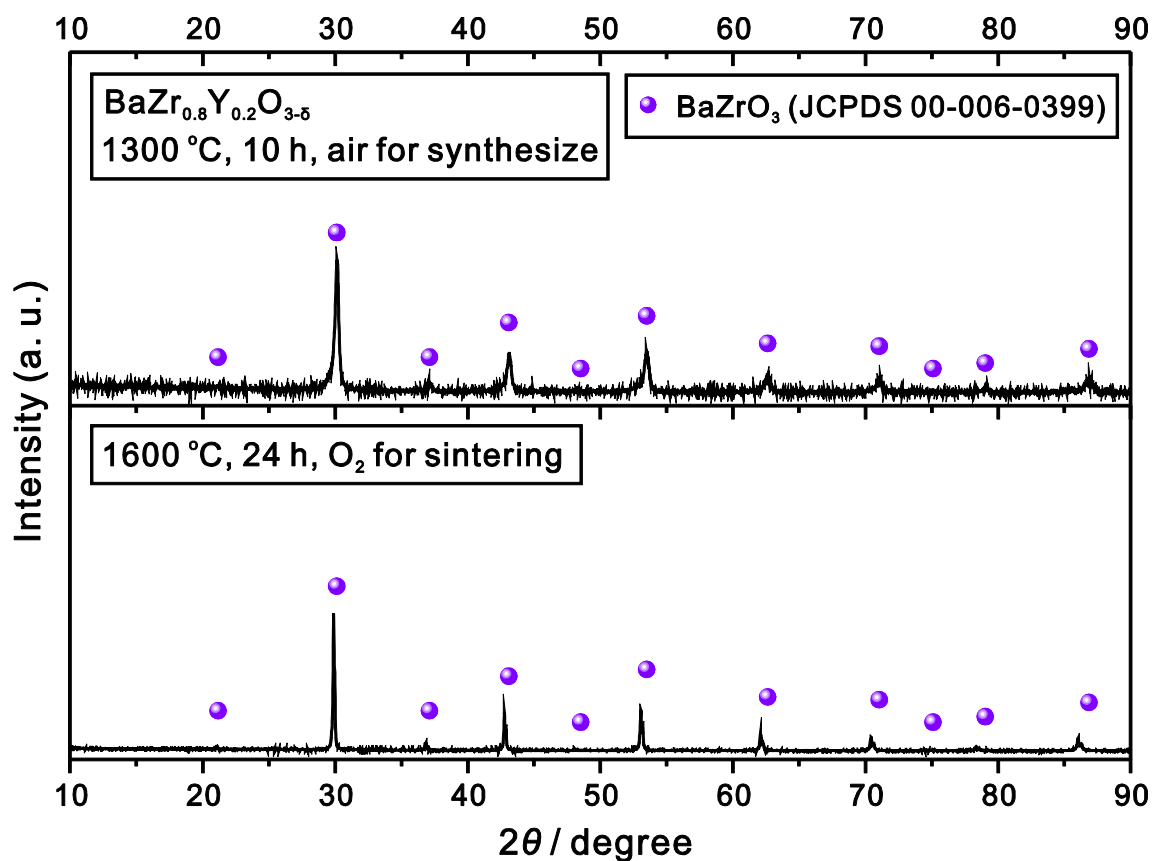


Fig. S4 Powder XRD patterns of BZY20 heat-treated at 1300 °C in air for 10 h and 1600 °C in O₂ for 24 h for synthesizing and sintering, respectively. Only the peaks belonging to a single perovskite phase were observed after both the heat-treatment.

STEM-EDS was applied to determine the local composition of crystal grains. In order to avoid the interference between different grains, single grains without overlapping with others were preferred for STEM-EDS analysis. Examples on the STEM-EDS analysis on BZY20 finally heat-treated at 1300 and 1600 °C are given in **Fig. S5**, **S6**, and **Table S2**, **S3**.

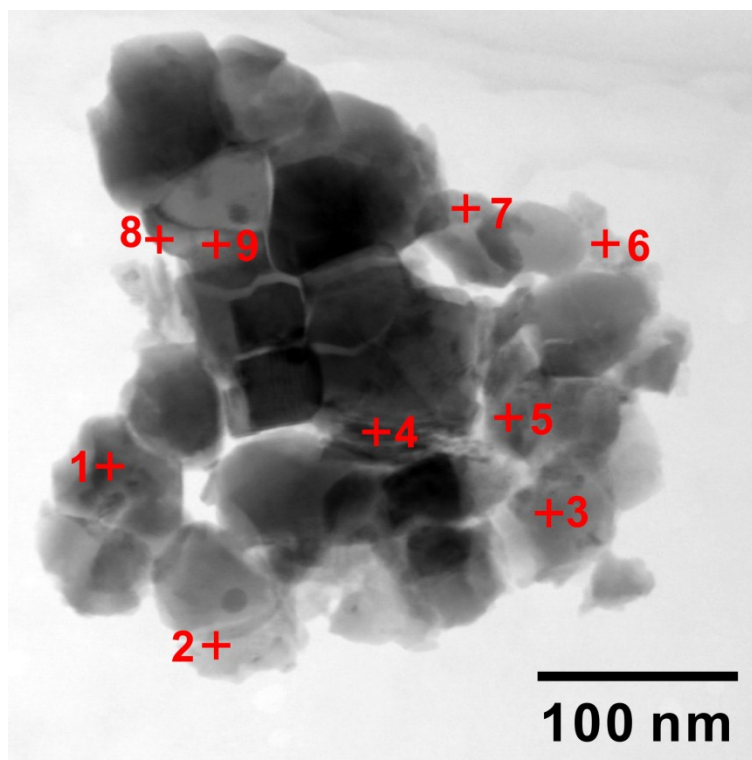


Fig. S5 Positions for STEM-EDS point-analysis on BZY20 finally heat-treated at 1300 °C in ambient air for 10h, and pulverized by ball-milling for 100 h.

Table S2 STEM-EDS point-analysis results on BZY20 which was finally heat-treated at 1300 °C in ambient atmosphere for 10 h, and pulverized by ball-milling for 100 h. The numbers are corresponding to the positions marked in **Fig. S5**.

Number	Cation ratio / at%			Number	Cation ratio / at%		
	Ba	Zr	Y		Ba	Zr	Y
1	51.57	45.05	3.37	6	44.47	44.41	11.12
2	50.98	39.71	9.31	7	52.70	34.67	12.63
3	51.59	43.56	4.85	8	51.44	46.82	1.75
4	14.38	43.48	42.15	9	49.41	48.36	2.23
5	54.42	37.00	8.58				

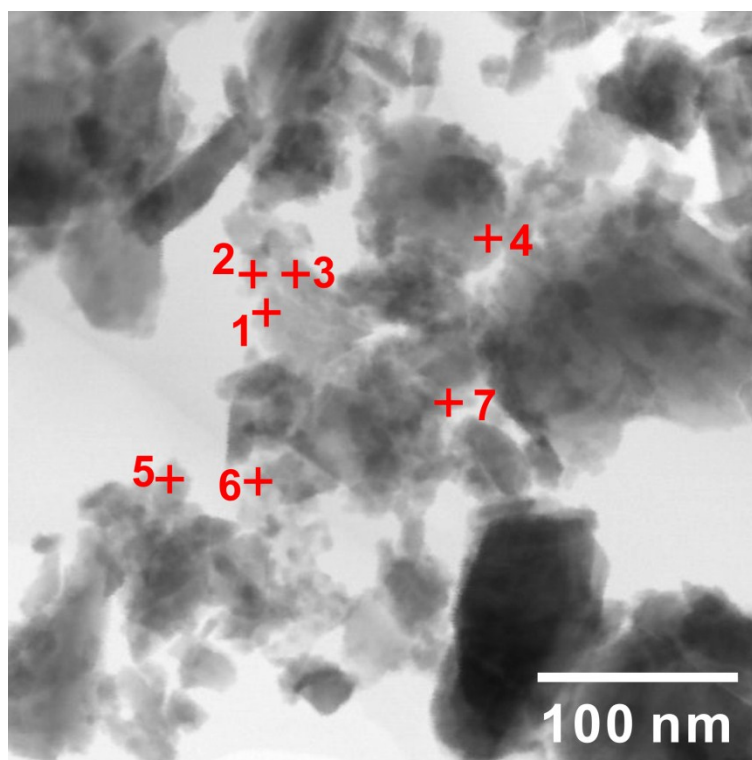


Fig. S6 Positions for STEM-EDS point-analysis on BZY20 finally heat-treated at 1600 °C in O₂ for 24 h, and pulverized by ball-milling for 50 h.

Table S3 STEM-EDS point-analysis results on BZY20 which was finally heat-treated at 1600 °C in O₂ for 24 h, and pulverized by ball-milling for 50 h. The numbers are corresponding to the positions marked in **Fig. S6**.

Number	Cation ratio / at%			Number	Cation ratio / at%		
	Ba	Zr	Y		Ba	Zr	Y
1	46.18	45.05	8.77	5	51.76	40.21	8.04
2	43.83	46.44	9.74	6	47.49	38.92	13.59
3	51.84	38.33	9.83	7	49.91	41.70	8.39
4	45.00	43.06	11.94				