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Electronic Supplementary Information (ESI)

Selecting Best Dopant Site in Proton Conducting Pyrochlore Oxides $La_2(Nb_{1-x}Y_x)_2O_{7-\delta}$ *via* Probing Hydration-Induced Local Distortion

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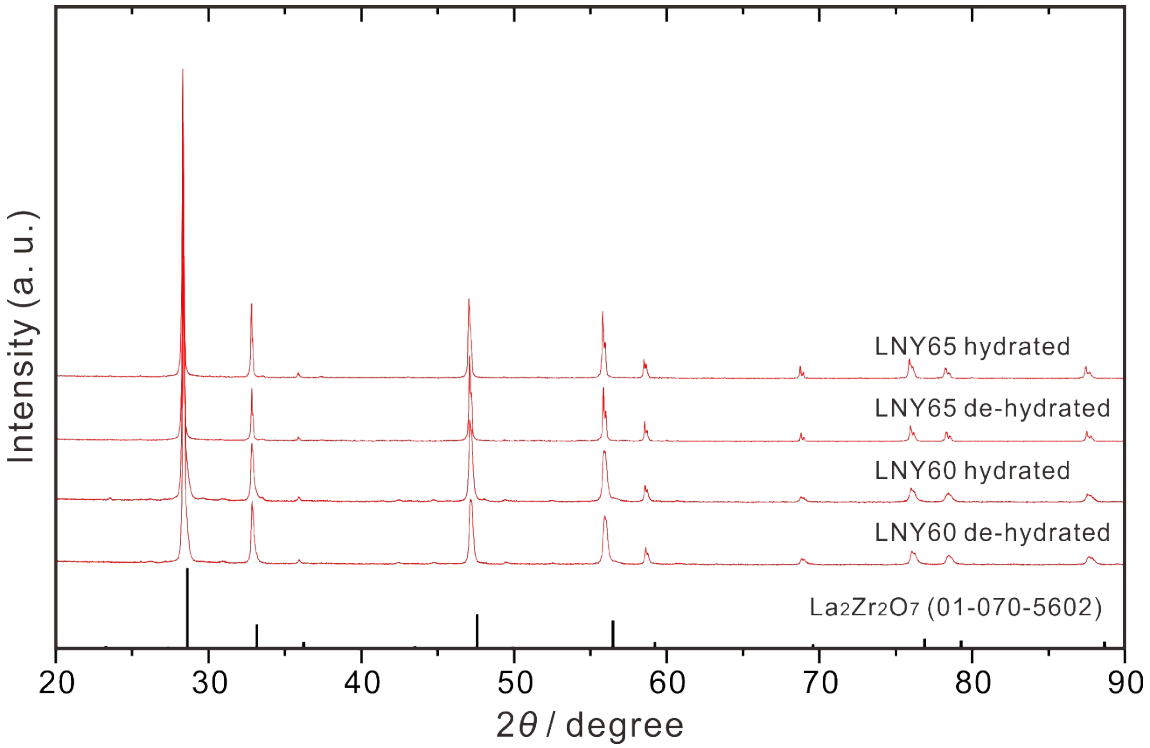

Fig. S1 Powder XRD patterns of hydrated and de-hydrated $La_2(Nb_{0.4}Y_{0.6})_2O_{7-\delta}$ (LNY60) and $La_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$ (LNY65) samples. The hydrated sample were prepared by annealing in wet argon with the partial pressure of water vapor of 0.05 atm at 300 °C for 5 days. The dehydrated samples were prepared by annealing at 1000 °C in dry Ar with water vapor lower than 0.3 ppm.

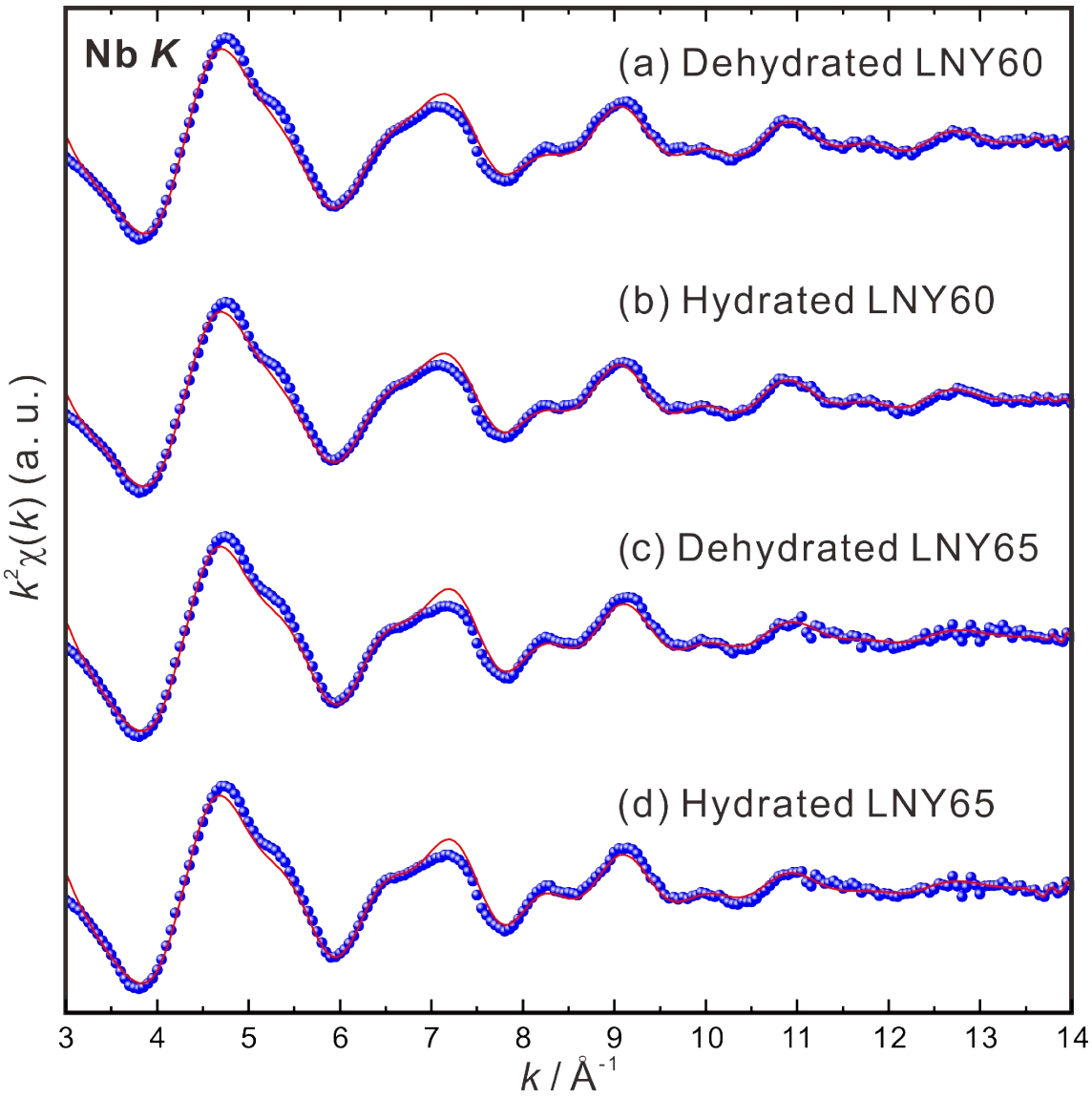

Fig. S2 Nb *K*-edge EXAFS data (circles) and best fit (red line) of (a) hydrated $La_2(Nb_{0.4}Y_{0.6})_2O_{7-\delta}$ (LNY60), (b) dehydrated LNY60, (c) hydrated $La_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$ (LNY65), and (d) dehydrated LNY65. The hydrated sample were prepared by annealing in wet argon with the partial pressure of water vapor of 0.05 atm at 300 °C for 5 days. The dehydrated samples were prepared by annealing at 1000 °C in dry Ar with water vapor lower than 0.3 ppm. The EXAFS spectra were collected at 10 K in vacuum.

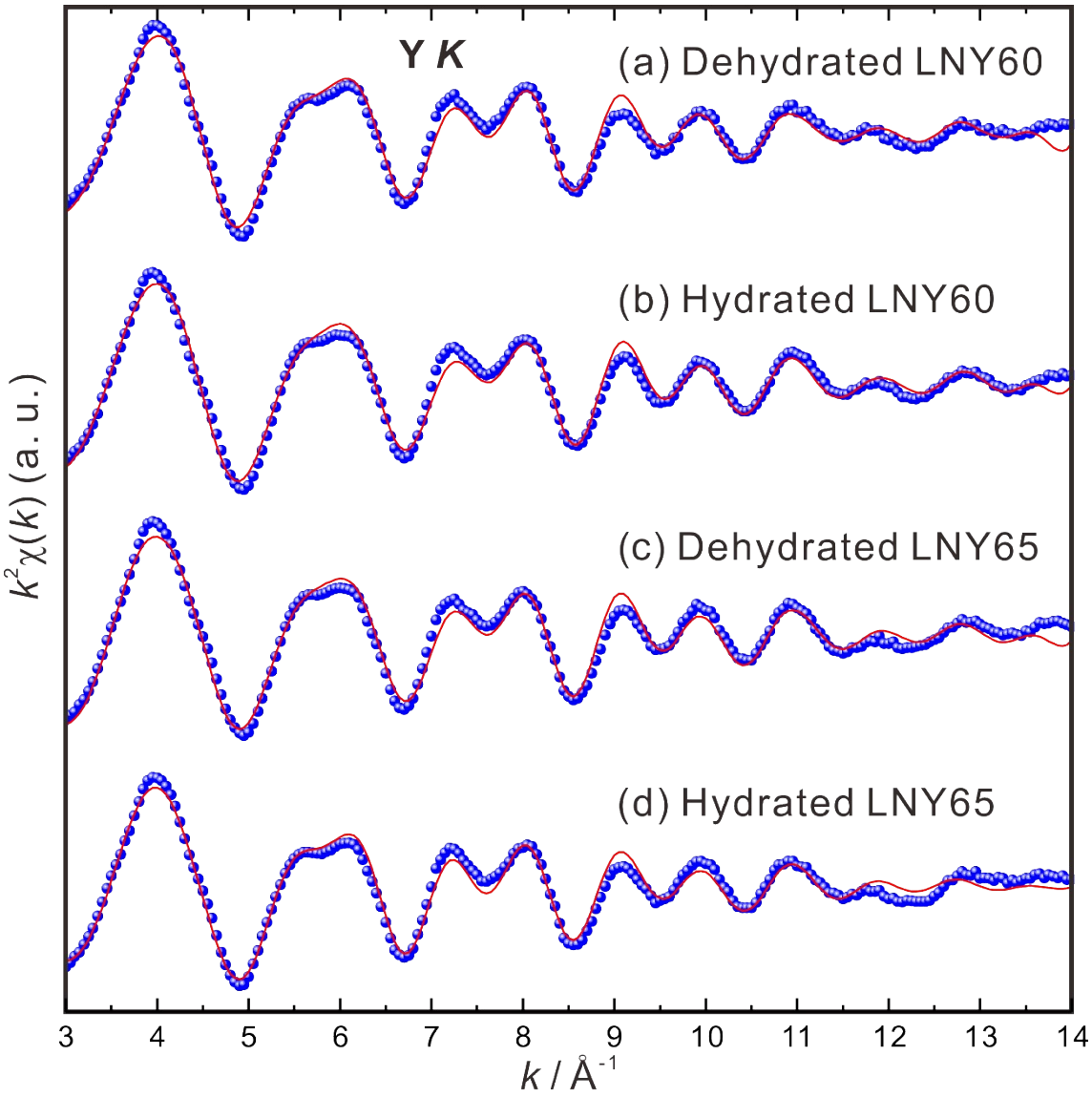

Fig. S3 Y *K*-edge EXAFS data (circles) and best fit (red line) of (a) hydrated $La_2(Nb_{0.4}Y_{0.6})_2O_{7-\delta}$ (LNY60), (b) dehydrated LNY60, (c) hydrated $La_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$ (LNY65), and (d) dehydrated LNY65. The hydrated sample were prepared by annealing in wet argon with the partial pressure of water vapor of 0.05 atm at 300 °C for 5 days. The dehydrated samples was annealed at 1000 °C in dry Ar with water vapor lower than 0.3 ppm. The EXAFS spectra were collected at 10 K in vacuum.

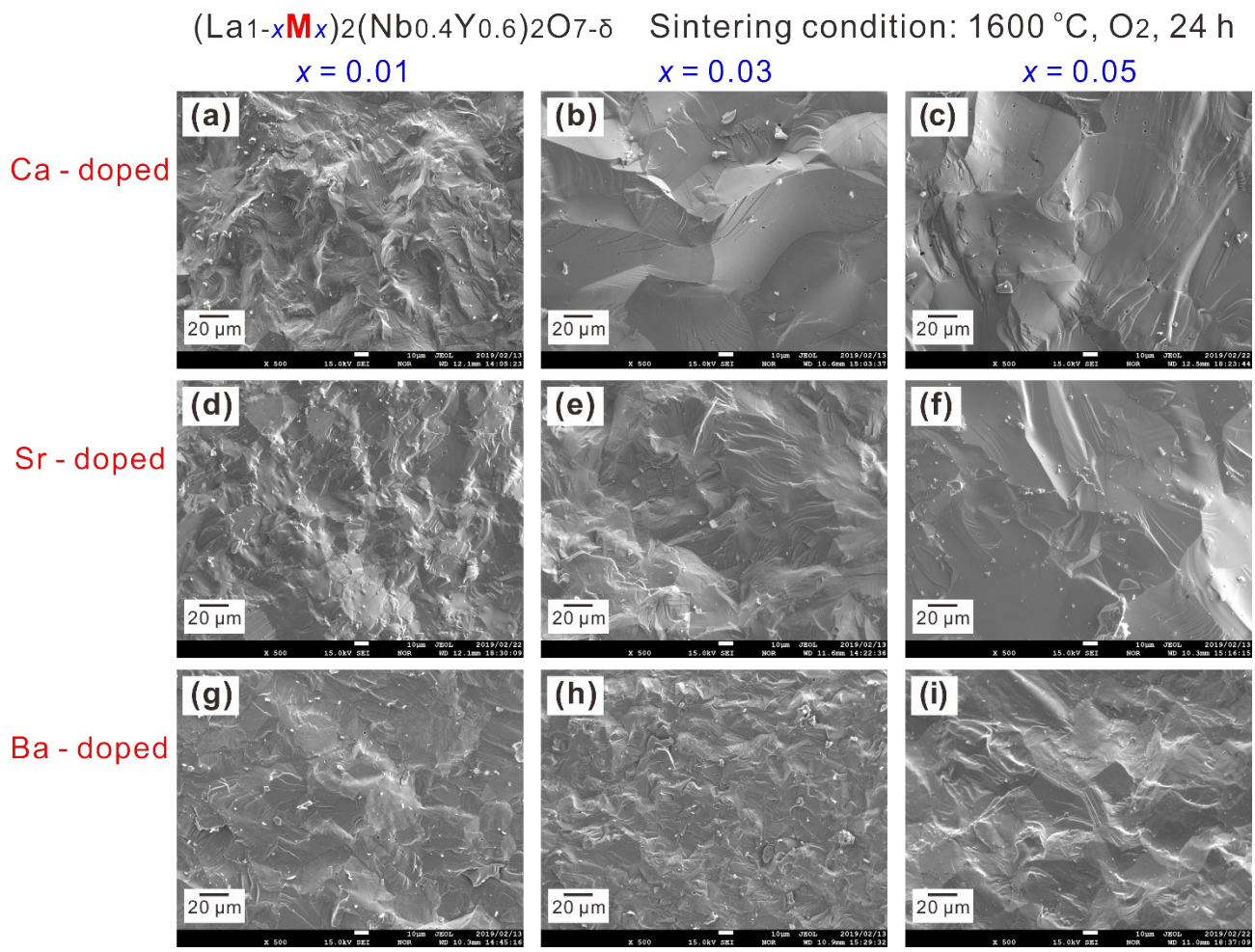

Fig. S4 EPMA second electron images of $(La_{1-x}Ca_x)_2(Nb_{0.4}Y_{0.6})_2O_{7-\delta}$ with (a) $x = 0.01$, (b) $x = 0.03$ and (c) $x = 0.05$, $(La_{1-x}Sr_x)_2(Nb_{0.4}Y_{0.6})_2O_{7-\delta}$ with (d) $x = 0.01$, (e) $x = 0.03$ and (f) $x = 0.05$, and $(La_{1-x}Ba_x)_2(Nb_{0.4}Y_{0.6})_2O_{7-\delta}$ with (g) $x = 0.01$, (h) $x = 0.03$ and (i) $x = 0.05$, which were sintered at 1600 °C in oxygen for 24 h.

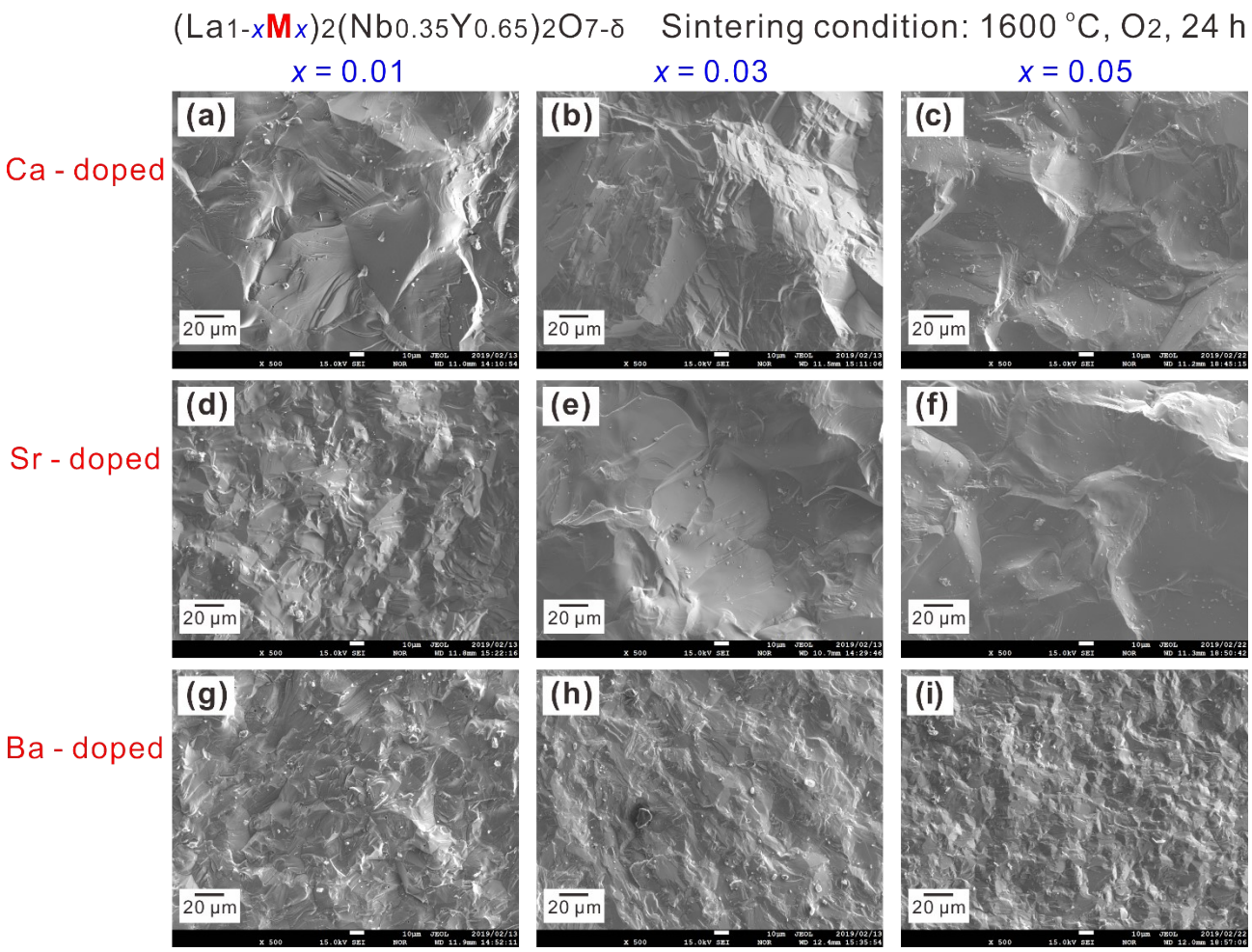

Fig. S5 EPMA second electron images of $(La_{1-x}Ca_x)_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$ with (a) x = 0.01, (b) x = 0.03 and (c) x = 0.05, $(La_{1-x}Sr_x)_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$ with (d) x = 0.01, (e) x = 0.03 and (f) x = 0.05, and $(La_{1-x}Ba_x)_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$ with (g) x = 0.01, (h) x = 0.03 and (i) x = 0.05, which were sintered at 1600 °C in oxygen for 24 h.

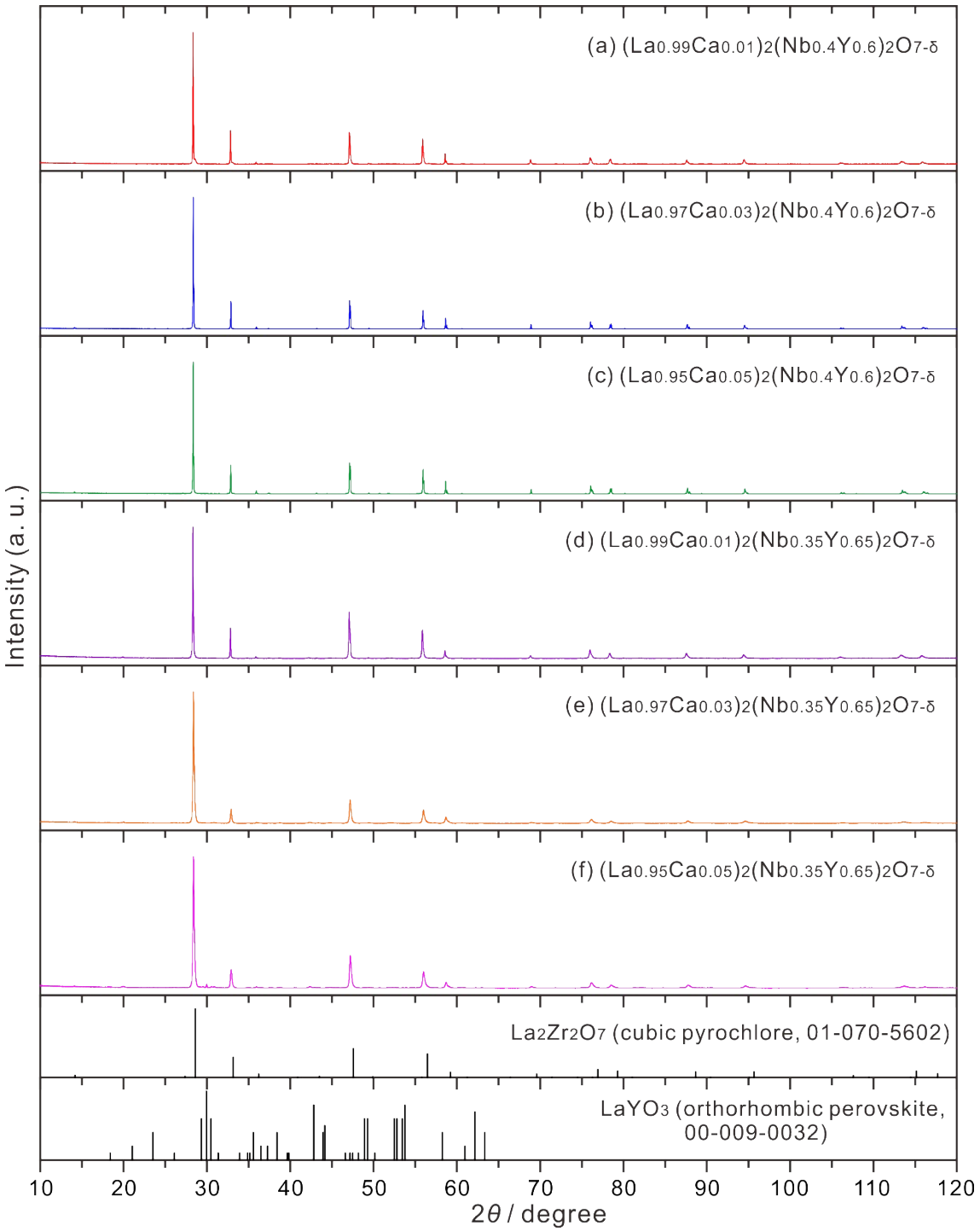

Fig. S6 Powder XRD patterns of the samples with the nominal compositions of (a) $(La_{0.99}Ca_{0.01})_2(Nb_{0.4}Y_{0.6})_2O_{7-\delta}$, (b) $(La_{0.97}Ca_{0.03})_2(Nb_{0.4}Y_{0.6})_2O_{7-\delta}$, (c) $(La_{0.95}Ca_{0.05})_2(Nb_{0.4}Y_{0.6})_2O_{7-\delta}$, (d) $(La_{0.99}Ca_{0.01})_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$, (e) $(La_{0.97}Ca_{0.03})_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$, (f) $(La_{0.95}Ca_{0.05})_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$, which were sintered at 1600 °C in oxygen for 24 h. The XRD patterns were collected with Cu *K*α1 monochromatic X-ray source.

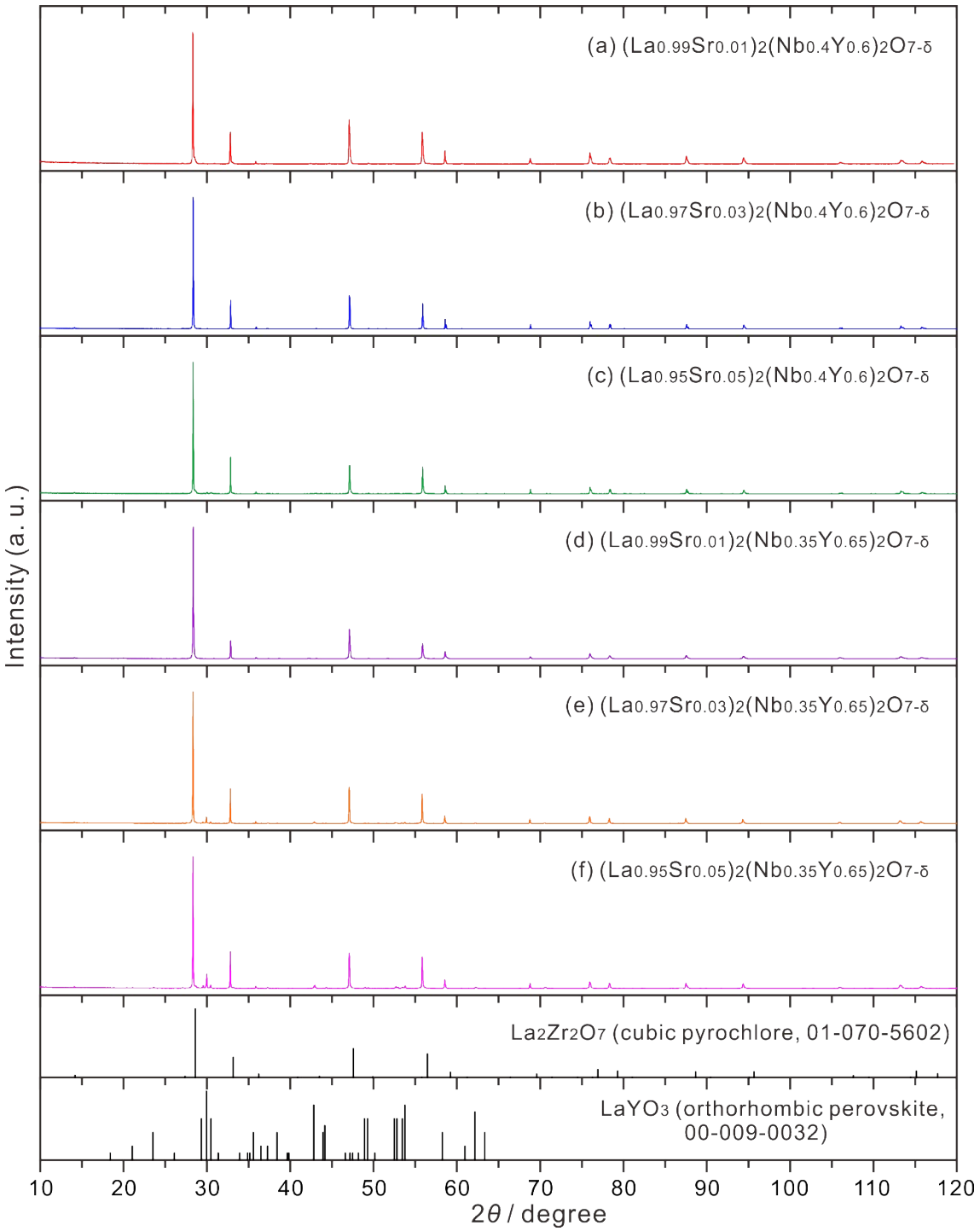

Fig. S7 Powder XRD patterns of the samples with the nominal compositions of (a) $(La_{0.99}Sr_{0.01})_2(Nb_{0.4}Y_{0.6})_2O_{7-\delta}$, (b) $(La_{0.97}Sr_{0.03})_2(Nb_{0.4}Y_{0.6})_2O_{7-\delta}$, (c) $(La_{0.95}Sr_{0.05})_2(Nb_{0.4}Y_{0.6})_2O_{7-\delta}$, (d) $(La_{0.99}Sr_{0.01})_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$, (e) $(La_{0.97}Sr_{0.03})_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$, (f) $(La_{0.95}Sr_{0.05})_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$, which were sintered at 1600 °C in oxygen for 24 h. The XRD patterns were collected with Cu *K*α1 monochromatic X-ray source.

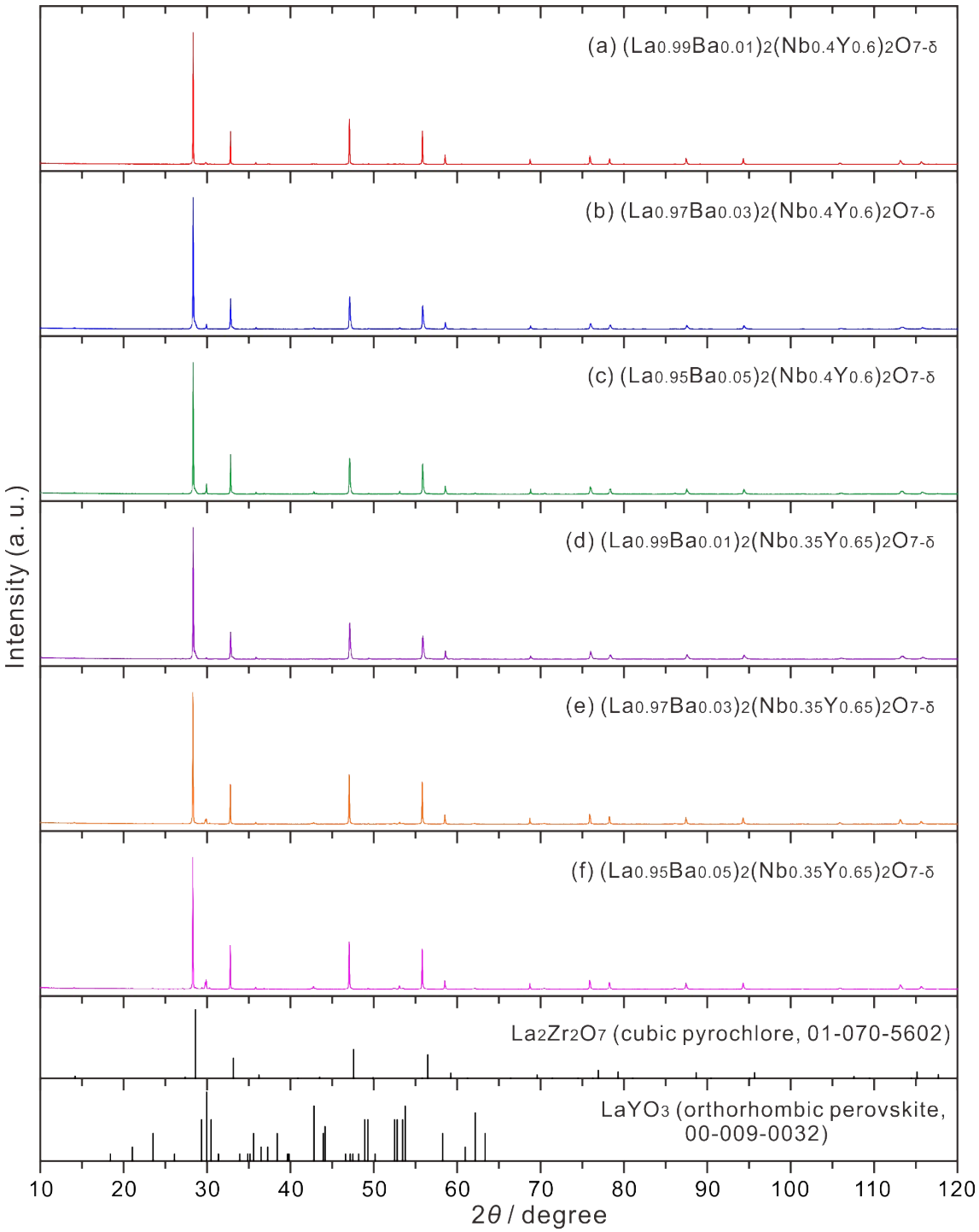

Fig. S8 Powder XRD patterns of the samples with the nominal compositions of (a) $(La_{0.99}Ba_{0.01})_2(Nb_{0.4}Y_{0.6})_2O_{7-\delta}$, (b) $(La_{0.97}Ba_{0.03})_2(Nb_{0.4}Y_{0.6})_2O_{7-\delta}$, (c) $(La_{0.95}Ba_{0.05})_2(Nb_{0.4}Y_{0.6})_2O_{7-\delta}$, (d) $(La_{0.99}Ba_{0.01})_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$, (e) $(La_{0.97}Ba_{0.03})_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$, (f) $(La_{0.95}Ba_{0.05})_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$, which were sintered at 1600 °C in oxygen for 24 h. The XRD patterns were collected with Cu *K*α1 monochromatic X-ray source.

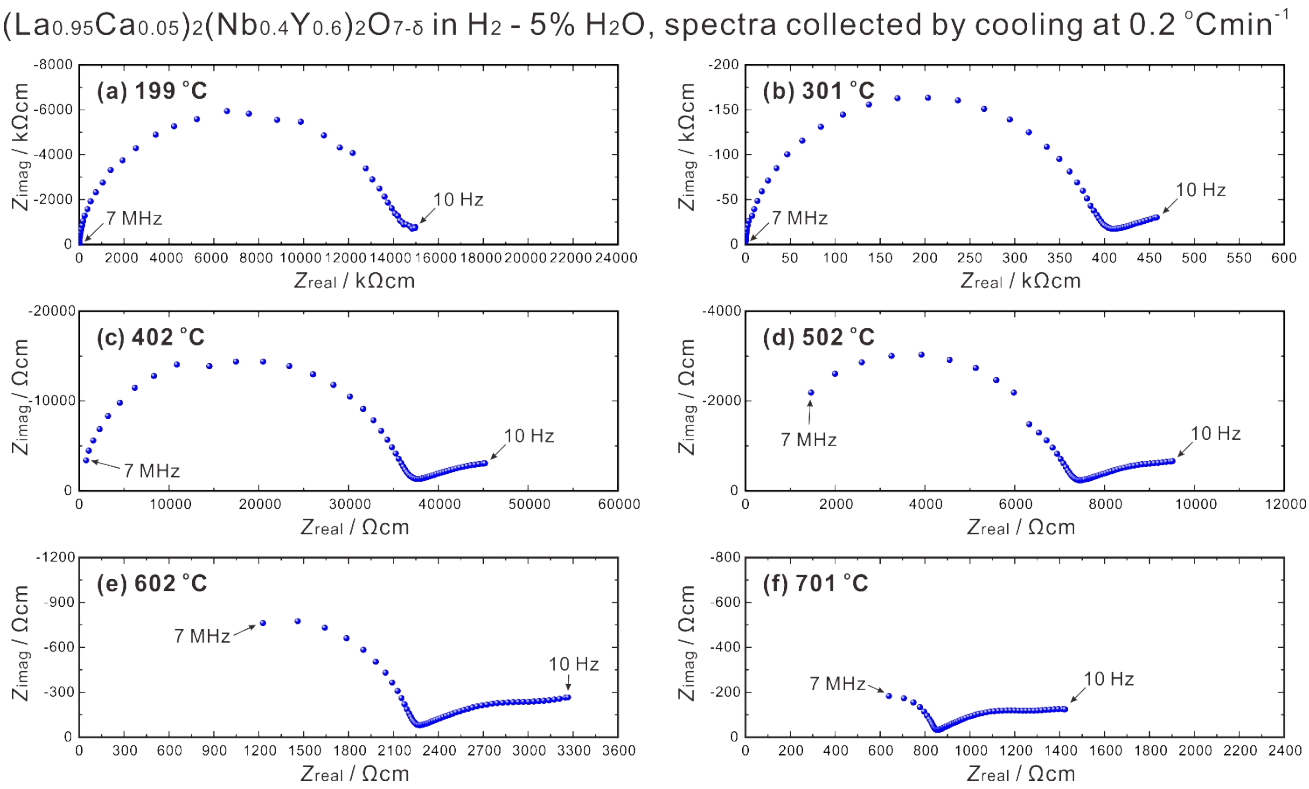

Fig. S9 AC impedance spectra of $(La_{0.95}Ca_{0.05})_2(Nb_{0.4}Y_{0.6})_2O_{7-\delta}$ collected in wet H_2 (p_{H_2O} = 0.05 atm) by cooling from 700 to 100 °C at 0.2 °Cmin^{-1}.

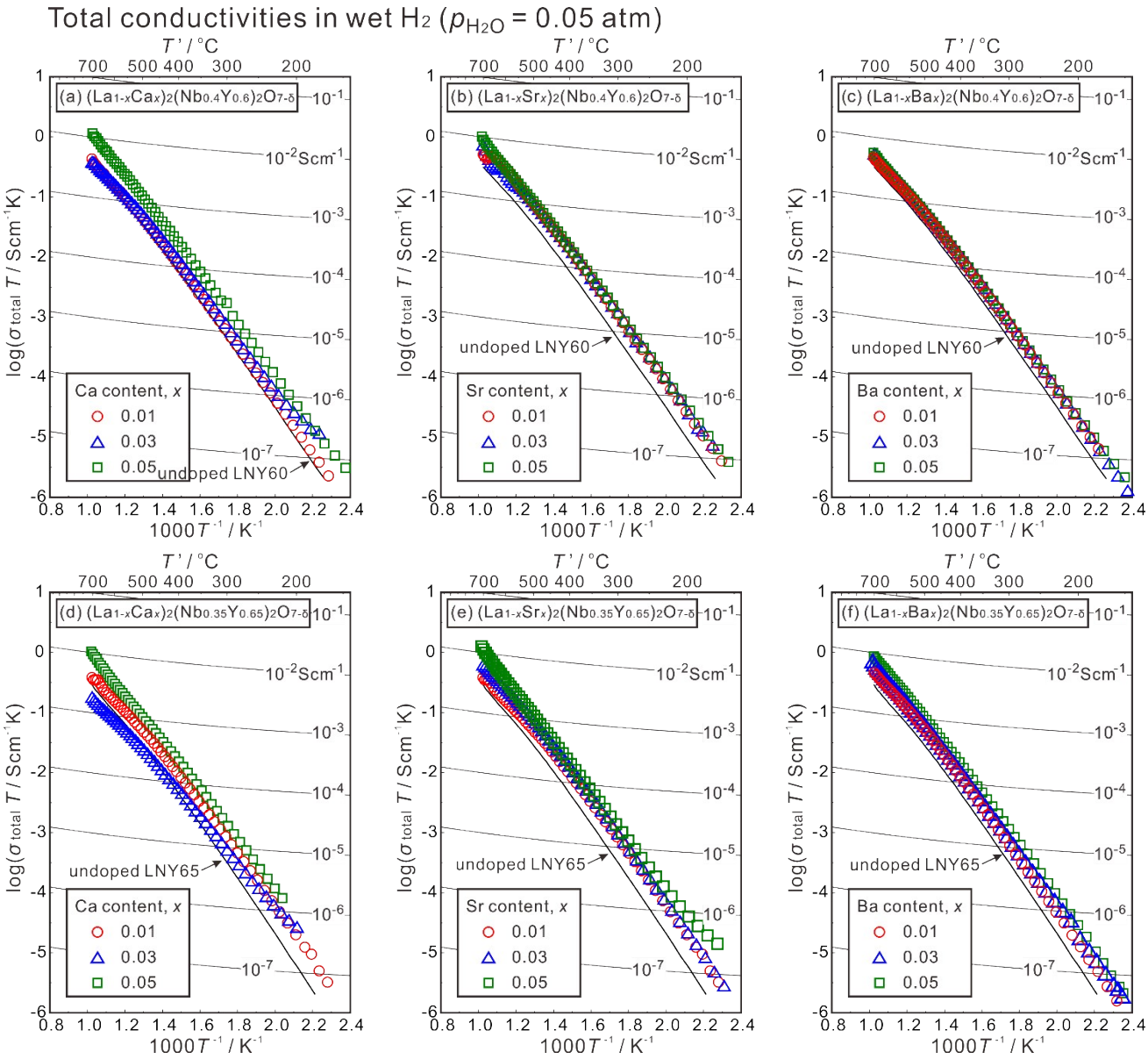

Fig. S10 Arrhenius plots of $La_2(Nb_{0.4}Y_{0.6})_2O_{7-\delta}$ doped with (a) Ca, (b) Sr and (c) Ba, and $La_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$ doped with (d) Ca, (e) Sr and (f) Ba in wet H_2 (p_{H_2O} = 0.05 atm).

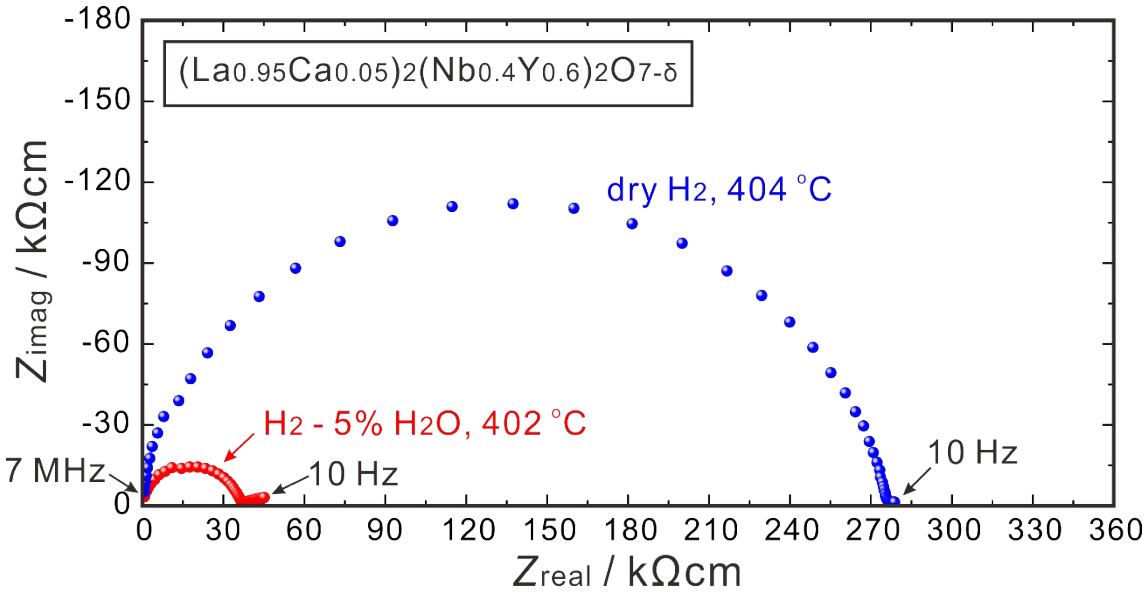

Fig. S11 AC impedance spectra of $(La_{0.95}Ca_{0.05})_2(Nb_{0.4}Y_{0.6})_2O_{7-\delta}$ collected in wet H_2 ($p_{H_2O} = 0.05$ atm) at 402 °C and in dry H_2 at 404 °C.

Table S1 Actual composition of the pyrochlore phases determined by EPMA-WDS point analysis. At least ten different places were probed randomly for each sample, and the average value was used here

Nominal composition	Actual composition of pyrochlore phase
$(La_{0.99}Ca_{0.01})_2(Nb_{0.40}Y_{0.60})_2O_{7-\delta}$	$(La_{0.984}Ca_{0.010})_2(Nb_{0.404}Y_{0.596})_2O_{7-\delta}$
$(La_{0.97}Ca_{0.03})_2(Nb_{0.40}Y_{0.60})_2O_{7-\delta}$	$(La_{0.968}Ca_{0.030})_2(Nb_{0.404}Y_{0.596})_2O_{7-\delta}$
$(La_{0.95}Ca_{0.05})_2(Nb_{0.40}Y_{0.60})_2O_{7-\delta}$	$(La_{0.969}Ca_{0.051})_2(Nb_{0.404}Y_{0.596})_2O_{7-\delta}$
$(La_{0.99}Sr_{0.01})_2(Nb_{0.40}Y_{0.60})_2O_{7-\delta}$	$(La_{1.001}Sr_{0.008})_2(Nb_{0.403}Y_{0.597})_2O_{7-\delta}$
$(La_{0.97}Sr_{0.03})_2(Nb_{0.40}Y_{0.60})_2O_{7-\delta}$	$(La_{0.993}Sr_{0.026})_2(Nb_{0.404}Y_{0.596})_2O_{7-\delta}$
$(La_{0.95}Sr_{0.05})_2(Nb_{0.40}Y_{0.60})_2O_{7-\delta}$	$(La_{1.025}Sr_{0.029})_2(Nb_{0.410}Y_{0.590})_2O_{7-\delta}$
$(La_{0.99}Ba_{0.01})_2(Nb_{0.40}Y_{0.60})_2O_{7-\delta}$	$(La_{1.001}Ba_{0.004})_2(Nb_{0.403}Y_{0.597})_2O_{7-\delta}$
$(La_{0.97}Ba_{0.03})_2(Nb_{0.40}Y_{0.60})_2O_{7-\delta}$	$(La_{0.960}Ba_{0.003})_2(Nb_{0.403}Y_{0.597})_2O_{7-\delta}$
$(La_{0.95}Ba_{0.05})_2(Nb_{0.40}Y_{0.60})_2O_{7-\delta}$	$(La_{1.021}Ba_{0.005})_2(Nb_{0.397}Y_{0.603})_2O_{7-\delta}$
$(La_{0.99}Ca_{0.01})_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$	$(La_{0.990}Ca_{0.010})_2(Nb_{0.354}Y_{0.646})_2O_{7-\delta}$
$(La_{0.97}Ca_{0.03})_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$	$(La_{0.971}Ca_{0.030})_2(Nb_{0.353}Y_{0.647})_2O_{7-\delta}$
$(La_{0.95}Ca_{0.05})_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$	$(La_{0.950}Ca_{0.052})_2(Nb_{0.354}Y_{0.646})_2O_{7-\delta}$
$(La_{0.99}Sr_{0.01})_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$	$(La_{0.999}Sr_{0.009})_2(Nb_{0.354}Y_{0.646})_2O_{7-\delta}$
$(La_{0.97}Sr_{0.03})_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$	$(La_{0.966}Sr_{0.017})_2(Nb_{0.370}Y_{0.630})_2O_{7-\delta}$
$(La_{0.95}Sr_{0.05})_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$	$(La_{1.017}Sr_{0.020})_2(Nb_{0.384}Y_{0.616})_2O_{7-\delta}$
$(La_{0.99}Ba_{0.01})_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$	$(La_{1.018}Ba_{0.003})_2(Nb_{0.355}Y_{0.645})_2O_{7-\delta}$
$(La_{0.97}Ba_{0.03})_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$	$(La_{1.058}Ba_{0.003})_2(Nb_{0.362}Y_{0.638})_2O_{7-\delta}$
$(La_{0.95}Ba_{0.05})_2(Nb_{0.35}Y_{0.65})_2O_{7-\delta}$	$(La_{1.027}Ba_{0.007})_2(Nb_{0.354}Y_{0.646})_2O_{7-\delta}$