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

Novel $ReBaCo_{1.5}Mn_{0.5}O_{5+\delta}$ (Re: La, Pr, Nd, Sm, Gd and Y) perovskite oxides: influence of manganese doping on crystal structure, oxygen nonstoichiometry, thermal expansion, transport properties, and application as cathode materials in Solid Oxide Fuel Cells

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Supplementary Information

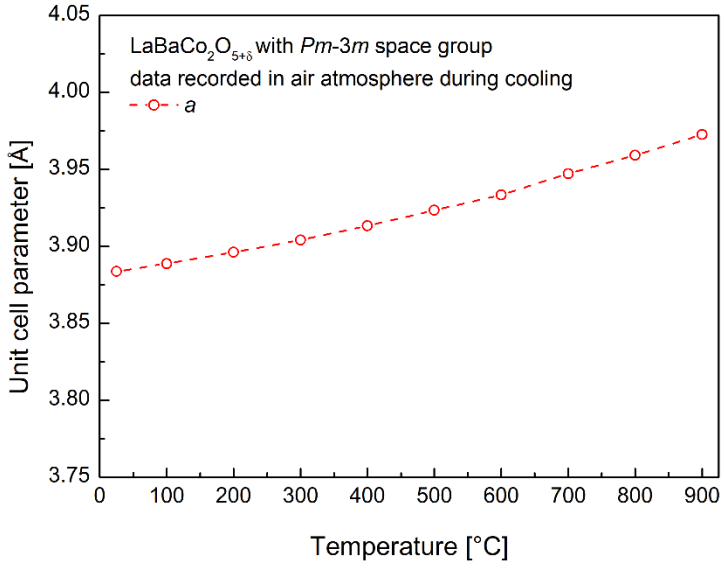

Fig. S1a. Temperature dependence of the unit cell parameter for $LaBaCo_2O_{5+\delta}$.

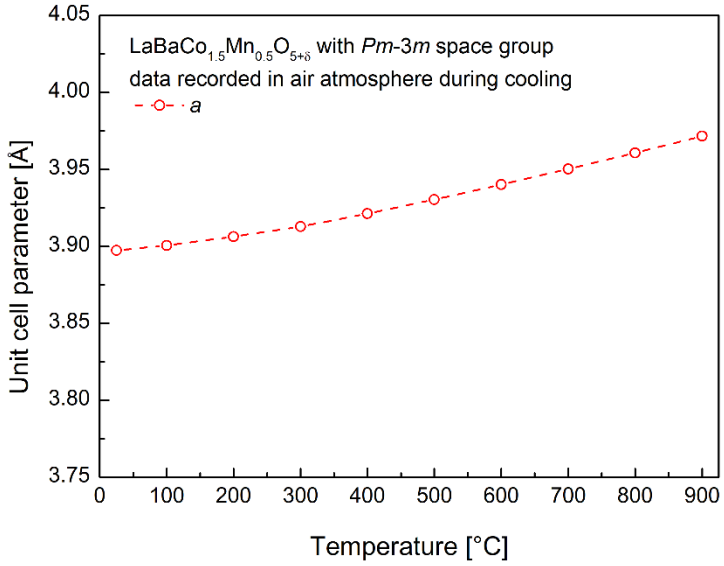

Fig. S1b. Temperature dependence of the unit cell parameter for $LaBaCo_{1.5}Mn_{0.5}O_{5+\delta}$.

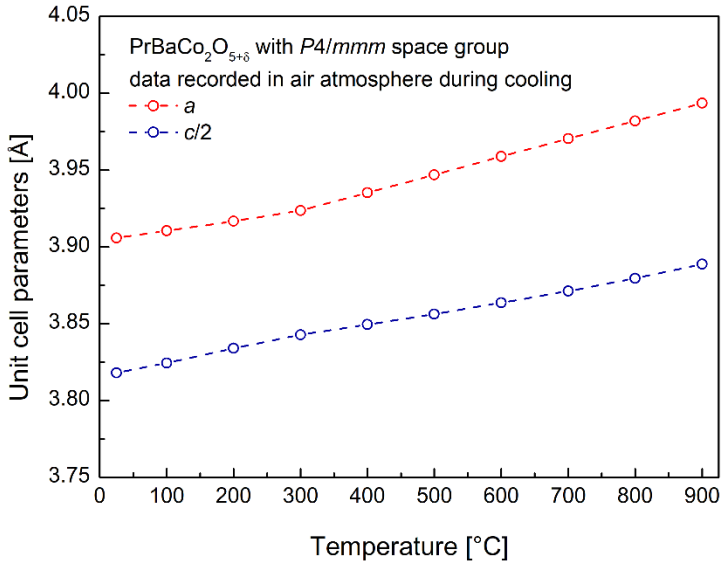

Fig. S2a. Temperature dependence of the unit cell parameters for $PrBaCo_2O_{5+\delta}$.

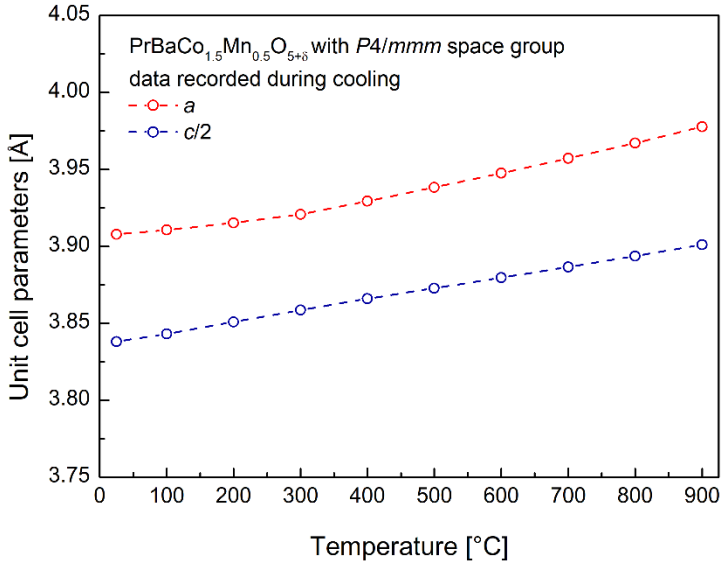

Fig. S2b. Temperature dependence of the unit cell parameters for $PrBaCo_{1.5}Mn_{0.5}O_{5+\delta}$.

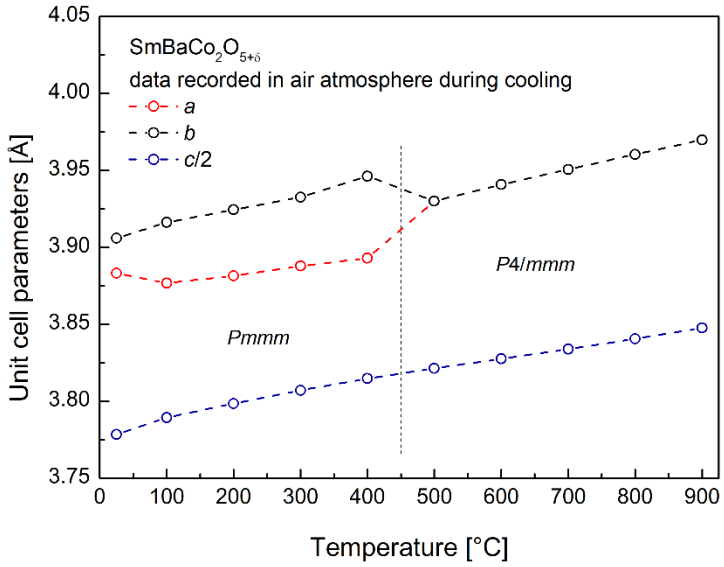

Fig. S3a. Temperature dependence of the unit cell parameters for $SmBaCo_2O_{5+\delta}$.

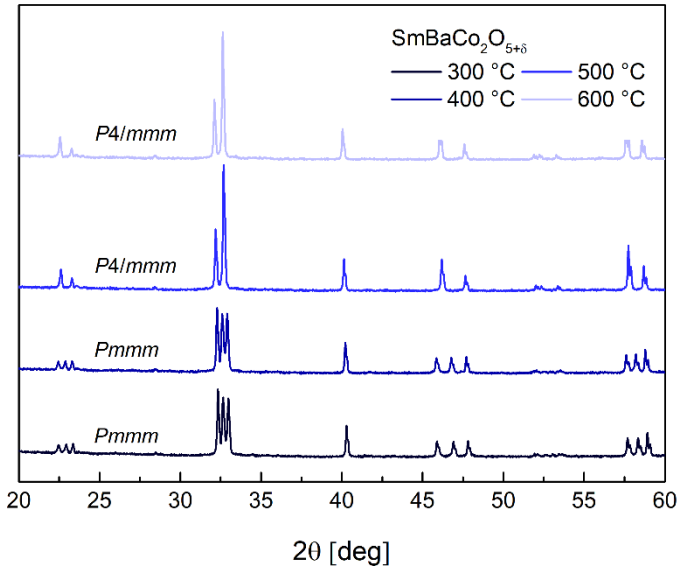

Fig. S3b. Selected range of XRD data for $SmBaCo_2O_{5+\delta}$ recorded at different temperatures.

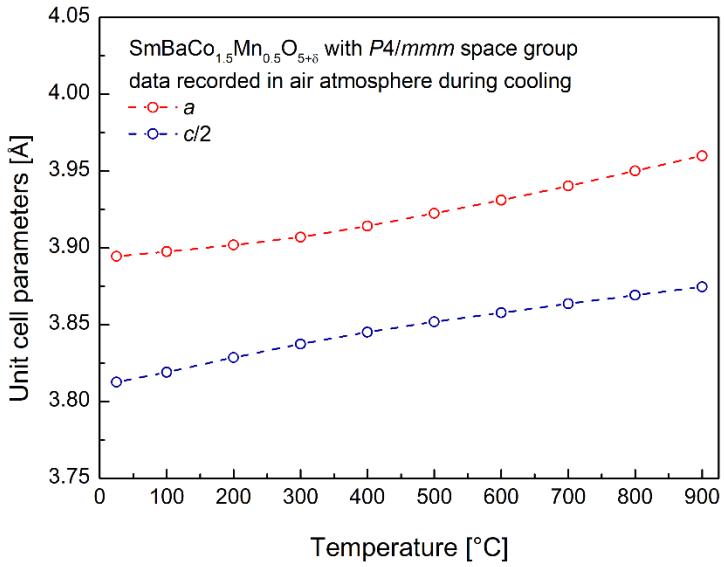

Fig. S3c. Temperature dependence of the unit cell parameters for $SmBaCo_{1.5}Mn_{0.5}O_{5+\delta}$.

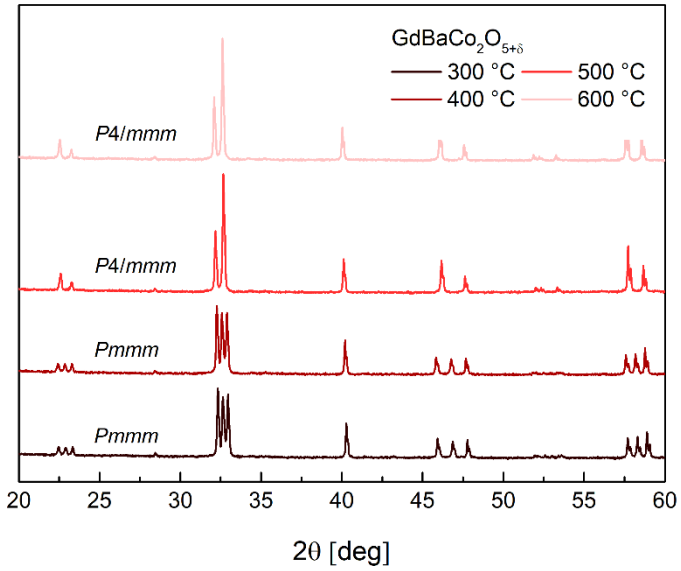

Fig. S4. Selected range of XRD data for $GdBaCo_2O_{5+\delta}$ recorded at different temperatures.

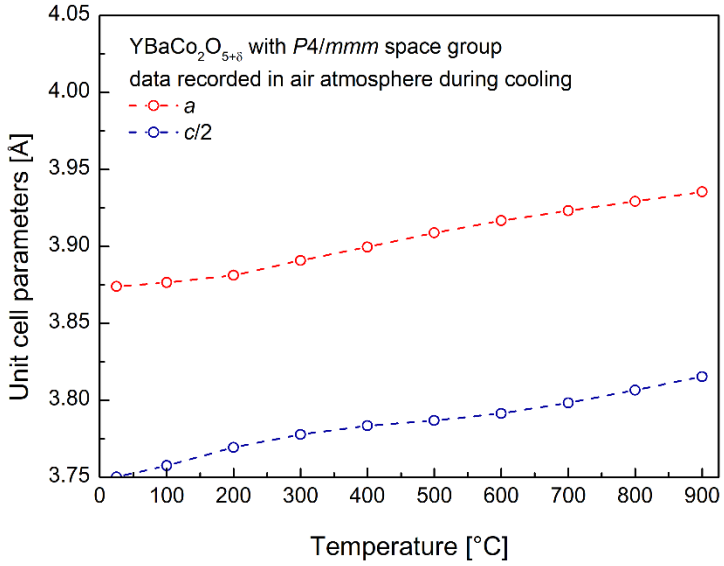

Fig. S5a. Temperature dependence of the unit cell parameters for $YBaCo_2O_{5+\delta}$.

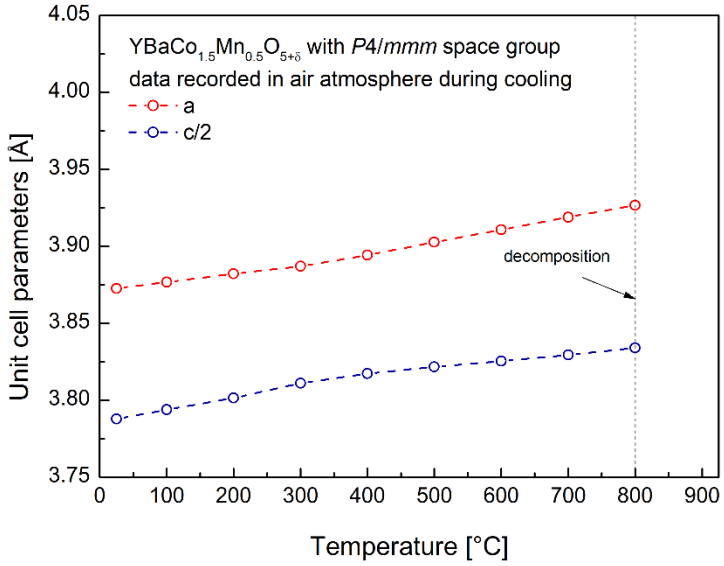

Fig. S5b. Temperature dependence of the unit cell parameters for $YBaCo_{1.5}Mn_{0.5}O_{5+\delta}$.

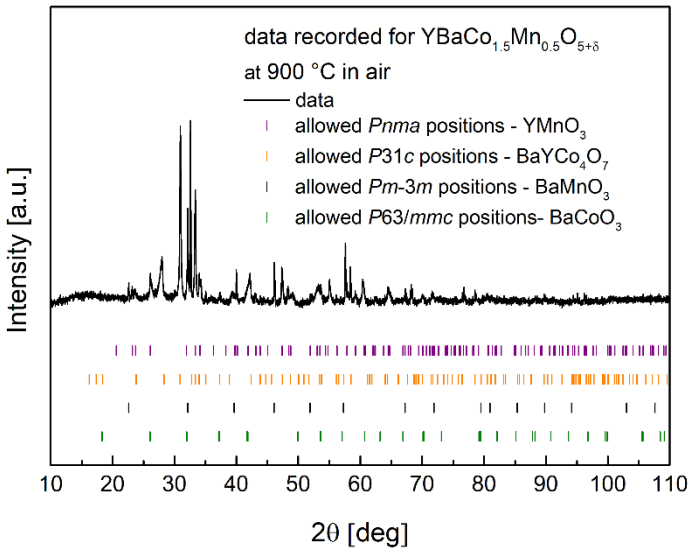

Fig. S5c. Decomposition of $YBaCo_{1.5}Mn_{0.5}O_{5+\delta}$ as visible in HT-XRD measurement at 900 °C.

Tab. S1. Values of the oxygen content, calculated for 600, 700, 800 and 900 °C for $ReBaCo_2O_{5+\delta}$ and $ReBaCo_{1.5}Mn_{0.5}O_{5+\delta}$ oxides (±0.01).

	600 °C	**700 °C**	**800 °C**	**900 °C**
$ReBaCo_2O_{5+\delta}$				
La	5.74	5.67	5.61	5.54
Pr	5.55	5.49	5.43	5.36
Nd	5.51	5.45	5.39	5.33
Sm	5.43	5.37	5.30	5.25
Gd	5.33	5.25	5.18	5.12
Y	5.06	5.02	4.99	4.99
$ReBaCo_{1.5}Mn_{0.5}O_{5+\delta}$				
La	5.84	5.79	5.74	5.69
Pr	5.74	5.70	5.65	5.60
Nd	5.71	5.67	5.62	5.57
Sm	5.62	5.57	5.51	5.46
Gd	5.54	5.49	5.43	5.38
Y	5.40	5.33	5.27	5.25

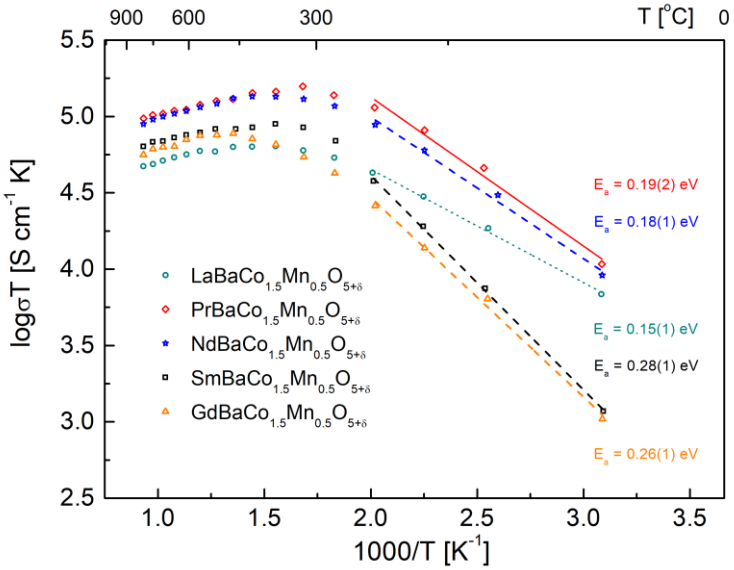

Fig. S6. Arrhenius-type plot used to calculate activation energy of the electrical conductivity of $ReBaCo_{1.5}Mn_{0.5}O_{5+\delta}$. E_a was estimated in 50-200 °C range.

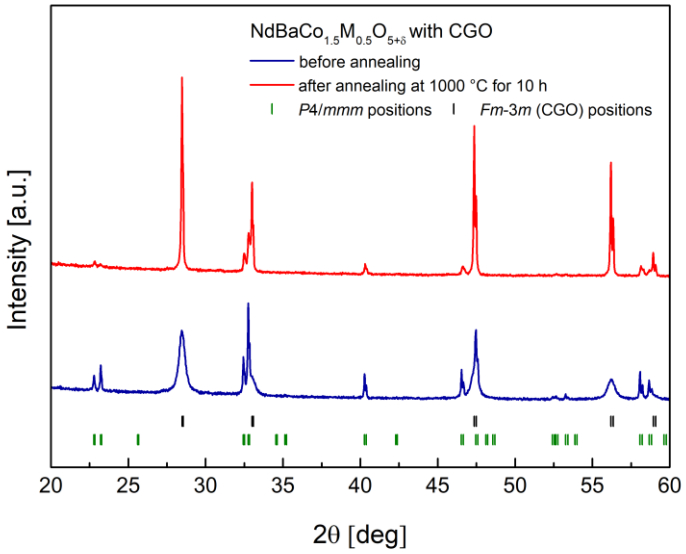

Fig. S7a. XRD patterns recorded for $NdBaCo_{1.5}Mn_{0.5}O_{5+\delta}$ mixed with CGO, before and after annealing at 1000 °C. Please notice that CGO-related peaks become very narrow after heat treatment.

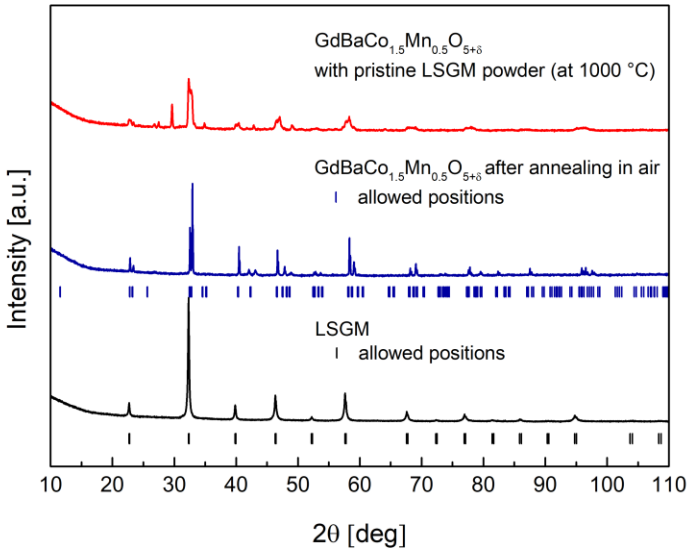

Fig. S7b. XRD studies of $GdBaCo_{1.5}Mn_{0.5}O_{5+\delta}$ stability in relation to LSGM electrolyte.

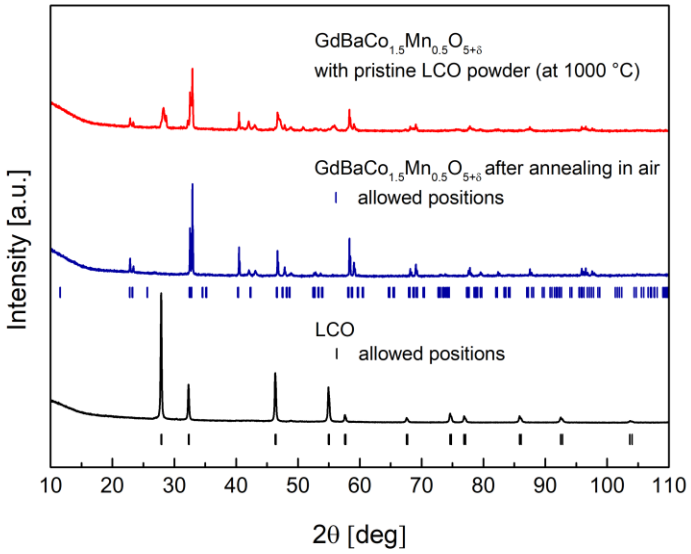

Fig. S7c. XRD studies of $GdBaCo_{1.5}Mn_{0.5}O_{5+\delta}$ stability in relation to LCO electrolyte.

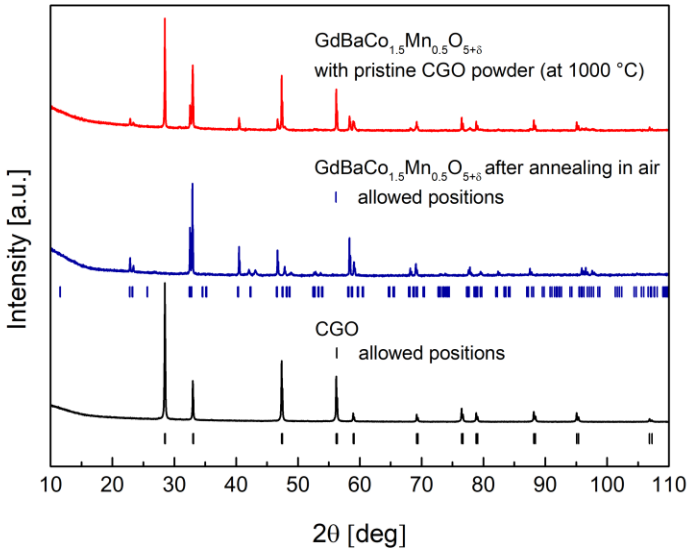

Fig. S7d. XRD studies of $GdBaCo_{1.5}Mn_{0.5}O_{5+\delta}$ stability in relation to CGO electrolyte.

Tab. S2. Refined values of the unit cell parameters and FWHM of the main perovskite peak for $NdBaCo_{1.5}Mn_{0.5}O_{5+\delta}$ and $GdBaCo_{1.5}Mn_{0.5}O_{5+\delta}$ oxides after stability tests with pristine LSGM, LCO and CGO electrolytes.

	a parameter [Å]	*c* parameter [Å]	FWHM [deg]
$NdBaCo_{1.5}Mn_{0.5}O_{5+\delta}$			
1000 °C, air	3.9003(1)	7.6562(1)	0.075
+ LSGM (1000 °C)	3.8469(1)	7.6852(1)	0.339
+ LCO (1000 °C)	3.9018(1)	7.6595(1)	0.104
+ CGO (1000 °C)	3.8977(1)	7.6592(1)	0.124
+ CGO (1100 °C)	3.8942(1)	7.6508(1)	0.172
+ CGO (1200 °C)	3.8954(1)	7.6550(1)	0.162
$GdBaCo_{1.5}Mn_{0.5}O_{5+\delta}$			
1000 °C, air	3.8877(1)	7.5996(1)	0.075
+ LSGM (1000 °C)	3.8746(1)	7.7209(1)	0.473
+ LCO (1000 °C)	3.8879(1)	7.6063(1)	0.117
+ CGO (1000 °C)	3.8862(1)	7.6010(1)	0.116
+ CGO (1100 °C)	3.8882(1)	7.6013(1)	0.154
+ CGO (1200 °C)	3.8900(1)	7.5989(1)	0.152

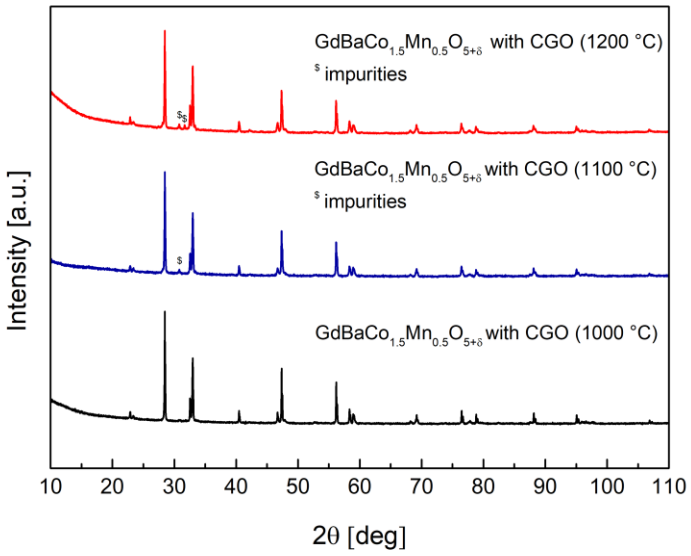

Fig. S8. XRD studies of $GdBaCo_{1.5}Mn_{0.5}O_{5+\delta}$ stability in relation to CGO electrolyte at different temperatures.

Tab. S3. Values of cathodic polarization R_p as a function of temperature determined for symmetrical cells with $NdBaCo_{1.5}Mn_{0.5}O_{5+\delta}$ cathode layers synthesized at different temperatures and sintered in 1000-1200 °C range.

sintering temperature [°C]	measurement temperature [°C]		
	800	850	900
synthesized at 1200 °C		**R_p [Ω cm^2]**	
1000	1.556	0.848	0.409
1100	0.346	0.206	0.122
1200	5.248	2.235	1.017
synthesized at 1000 °C		**R_p [Ω cm^2]**	
1050	0.420	0.238	0.139
1075	0.372	0.202	0.112
1100	0.117	0.070	**0.043**
1125	0.387	0.234	0.141

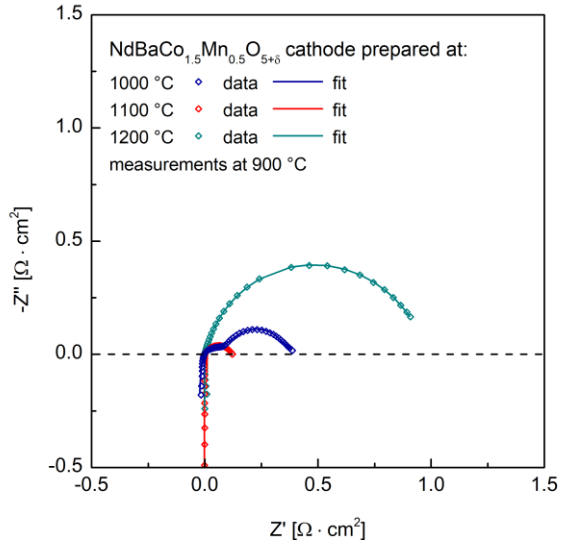

Fig. S9. Measured impedance data for symmetrical cells with $NdBaCo_{1.5}Mn_{0.5}O_{5+\delta}$ cathode synthesized at 1200 °C and prepared at different temperatures. Ohmic resistance was subtracted and the values were divided by two, due to the symmetric configuration, which allowed to estimate cathodic polarization R_p.