Supplementary Information

Crystal structure and surface characteristics of Sr-doped $GdBaCo_2O_{6-\delta}$ double perovskites: Oxygen evolution reaction and conductivity

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Table S1: Refined atomic parameters for GBCO. Occupancies were fixed to nominal values, with O3 and O4 fixed to values according to the titration results. B_{eq} for all oxygen ions were constrained to have the same value.

Site	*x*	*y*	*z*	B_{eq}	Occupancy
Gd1	0.5	0.2728(6)	0.5	1.1(2)	1
Ba1	0.5	0.2503(6)	0	0.6(1)	1
Co1	0	0.5	0.250(2)	0.6(3)	1
Co2	0	0	0.258(2)	0.4(2)	1
O1	0	0	0	2.0(3)	1
O2	0	0.5	0	2.0(3)	1
O3	0	0.5	0.5	2.0(3)	0.21
O4	0	0	0.5	2.0(3)	0.21
O5	0.5	0	0.307(6)	2.0(3)	1
O6	0.5	0.5	0.274(7)	2.0(3)	1
O7	0	0.240(4)	0.297(4)	2.0(3)	1

Table S2: Refined atomic parameters for GB9S1CO. Occupancies were fixed to nominal values, with O3 and O4 fixed to values according to the titration results. B_{eq} for all oxygen ions were constrained to have the same value.

Site	*x*	*y*	*z*	B_{eq}	Occupancy
Gd1	0.5	0.2708(6)	0.5	1.5(2)	1
Ba/Sr1	0.5	0.2516(7)	0	0.8(1)	0.9/0.1
Co1	0	0.5	0.247(2)	0.8(3)	1
Co2	0	0	0.255(2)	0.6(3)	1
O1	0	0	0	2.2(2)	1
O2	0	0.5	0	2.2(2)	1
O3	0	0.5	0.5	2.2(2)	0.28
O4	0	0	0.5	2.2(2)	0.28
O5	0.5	0	0.301(4)	2.2(2)	1
O6	0.5	0.5	0.255(9)	2.2(2)	1
O7	0	0.235(4)	0.298(2)	2.2(2)	1

Table S3: Refined atomic parameters for GB8S2CO. Occupancies were fixed to nominal values, with O4 fixed to the value according to the titration results. B_{eq} for all oxygen ions were constrained to have the same value.

Site	*x*	*y*	*z*	B_{eq}	Occupancy
Gd1	0.5	0.5	0.5	2.5(2)	1
Ba/Sr1	0.5	0.5	0	0.9(2)	0.8/0.2
Co1	0	0	0.251(2)	0.95(8)	1
O1	0	0	0	4.7(4)	1
O2	0.5	0	0.289(7)	4.7(4)	1
O3	0	0.5	0.301(6)	4.7(4)	1
O4	0	0	0.5	4.7(4)	0.38

Table S4: Refined atomic parameters for GB7S3CO. Occupancies were fixed to nominal values, with O4 fixed to the value according to the titration results. B_{eq} for all oxygen ions were constrained to have the same value.

Site	*x*	*y*	*z*	B_{eq}	Occupancy
Gd1	0.5	0.5	0.5	2.0(2)	1
Ba/Sr1	0.5	0.5	0	0.4(2)	0.7/0.3
Co1	0	0	0.251(2)	0.77(8)	1
O1	0	0	0	2.6(3)	1
O2	0.5	0	0.30(1)	2.6(3)	1
O3	0	0.5	0.29(1)	2.6(3)	1
O4	0	0	0.5	2.6(3)	0.51

Table S5: Refined atomic parameters for GB6S4CO. Occupancies were fixed to nominal values, with O3 fixed to the value according to the titration results. B_{eq} for all oxygen ions were constrained to have the same value.

Site	*x*	*y*	*z*	B_{eq}	Occupancy
Gd1	0.5	0.5	0.5	2.6(2)	1
Ba/Sr1	0.5	0.5	0	0.6(1)	0.6/0.4
Co1	0	0	0.253(1)	0.91(7)	1
O1	0	0	0	2.9(3)	1
O2	0.5	0	0.286(2)	2.9(3)	1
O3	0	0	0.5	2.9(3)	0.54

Table S6: Refined atomic parameters for GB5S5CO. Occupancies were fixed to nominal values, with O3 fixed to the value according to the titration results. B_{eq} for all oxygen ions were constrained to have the same value.

Site	*x*	*y*	*z*	B_{eq}	Occupancy
Gd1	0.5	0.5	0.5	2.1(2)	1
Ba/Sr1	0.5	0.5	0	0.4(2)	0.5/0.5
Co1	0	0	0.252(2)	0.82(8)	1
O1	0	0	0	4.4(4)	1
O2	0.5	0	0.287(2)	4.4(4)	1
O3	0	0	0.5	4.4(4)	0.55

Table S7: Co-O bond lengths, bond valence sums and Co oxidation state determined from titration for GBCO and GB9S1CO. <Co#-O> means the average of bond length of Co# polyhedron.

	GBCO	GB9S1CO
Co1 Polyhedron	**Distance (Å)**	**Distance (Å)**
Co1-O2	1.882(17)	1.864(18)
Co1-O3	1.885(17)	1.906(18)
Co1-O6 (x2)	1.948(6)	1.936(4)
Co1-O7 (x2)	2.06(3)	2.10(3)
<Co1-O>	1.96(5)	1.97(5)
BVS	2.52(3)	2.54(3)
Co2 Polyhedron	**Distance (Å)**	**Distance (Å)**
Co2-O4	1.825(14)	1.851(17)
Co2-O7 (x2)	1.91(3)	1.87(3)
Co2-O1	1.942(14)	1.919(17)
Co2-O5 (x2)	1.975(10)	1.966(7)
<Co2-O>	1.92(5)	1.91(5)
BVS	2.75(7)	2.98(8)
<BVS>	2.64(7)	2.76(8)
Co valence determined from titration	2.71(1)	2.78(1)

R_0 values used for the bond valence summations Co^{3+} – O = 1.70.

Table S8: Co-O bond lengths, bond valence sums and Co oxidation state determined from titration for GB8S2CO and GB7S3CO. <Co1-O> means the average of bond length of Co1 polyhedron.

	GB8S2CO	**GB7S3CO**
Co1 Polyhedron	**Distance (Å)**	**Distance (Å)**
Co1-O4	1.877(12)	1.879(12)
Co1-O1	1.894(12)	1.894(12)
Co1-O2 (x2)	1.955(10)	1.962(16)
Co1-O3 (x2)	1.978(11)	1.954(15)
<Co1-O>	1.94(3)	1.93(4)
BVS	2.77(3)	2.90(4)
Co valence determined from titration	2.88(1)	3.01(1)

R_0 values used for the bond valence summations Co^{3+} – O = 1.70

Table S9: Co-O bond lengths, bond valence sums and Co oxidation state determined from titration for GB6S4CO and GB5S5CO. <Co1-O> means the average of bond length of Co1 polyhedron.

	GB6S4CO	**GB5S5CO**
Co1 Polyhedron	**Distance (Å)**	**Distance (Å)**
Co1-O3	1.867(10)	1.868(12)
Co1-O1	1.905(10)	1.900(12)
Co1-O2 (x4)	1.946(4)	1.943(5)
<Co1-O>	1.926(15)	1.923(18)
BVS	2.98(2)	3.01(2)
Co valence determined from titration	3.04(1)	3.05(1)

R_0 values used for the bond valence summations Co^{3+} – O = 1.70

Table S10: Oxygen evolution reaction performance of the double perovskite-related materials measured at 1 mA cm^{-2}.

Catalyst	Potential (V vs RHE)	Catalyst loading (mg cm^{-2})	Scan rate (mV s^{-1})	Ref	Remarks
GB8S2CO	1.70	0.253	1	This work	6th cycle, mixed with nafion, iR compensated
GB7S3CO	1.71	0.253	1	This work	
GB6S4CO	1.69	0.253	1	This work	
$PrBaCo_2O_{5+\delta}$	1.54	0.25	10	[1]	2nd cycle, mixed with acetylene black and nafion, iR compensated
$HoBaCo_2O_{5+\delta}$	1.56	0.25	10	[1]	
$SmBaCo_2O_{5+\delta}$	1.57	0.25	10	[1]	
$GdBaCo_2O_{5+\delta}$	1.58	0.25	10	[1]	
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$	1.57	0.25	10	[1]	
$LaCoO_3$	1.64	0.25	10	[1]	
$PrBaCo_2O_{5+\delta}$	1.61	0.545	5	[2]	Mixed with acetylene black carbon and nafion
$PrBa_{0.75}Sr_{0.25}Co_2O_{5+\delta}$	1.58	0.545	5	[2]	
$PrBa_{0.5}Sr_{0.5}Co_2O_{5+\delta}$	1.55	0.545	5	[2]	
$PrBa_{0.25}Sr_{0.75}Co_2O_{5+\delta}$	1.55	0.545	5	[2]	
$PrSrCo_2O_{5+\delta}$	1.55	0.545	5	[2]	
$PrBaCo_2O_{5+\delta}$	1.66	0.202	10	[3]	Mixed with acetylene black carbon and nafion, iR compensated
$PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$	1.62	0.202	10	[3]	
$PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$	1.52-1.55	0.202	10	[3]	Nanofibers, mixed with acetylene black carbon and nafion, iR compensated

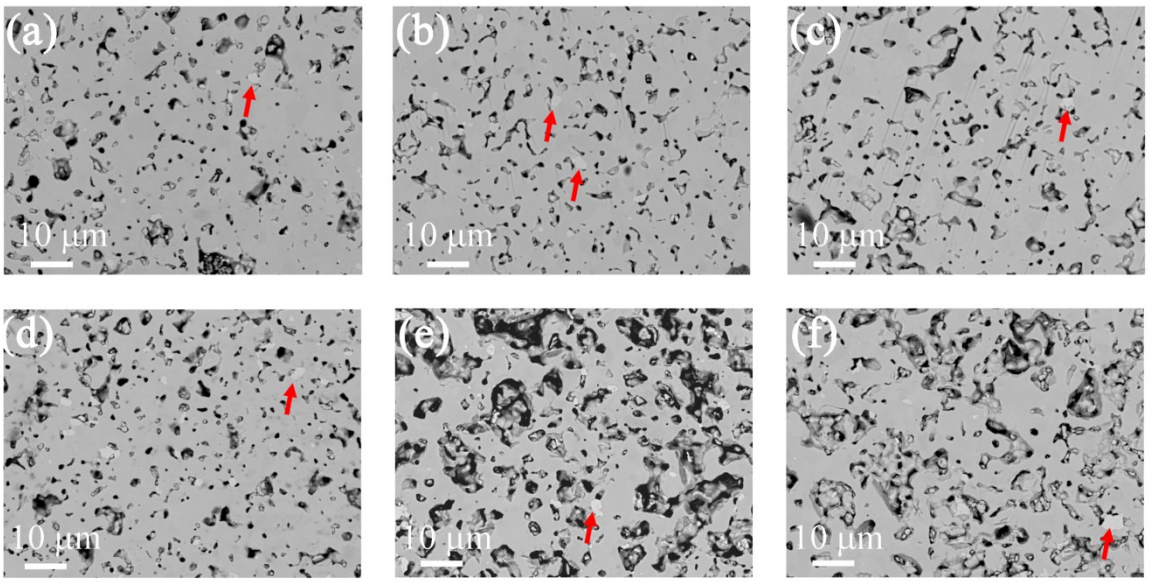

Figure S1: **Back-scattered electron (BSE) images of (a) GB8S2CO, (b) GB8S2CO-600C, (c) GB8S2CO-800C, (d) GB6S4CO, (e) GB6S4CO-600C, (f) GB6S4CO-800C. Brighter regions marked by red arrows were quantified as a single perovskite $Gd_{1.00(3)}Co_{0.97(3)}O_3$ phase.**

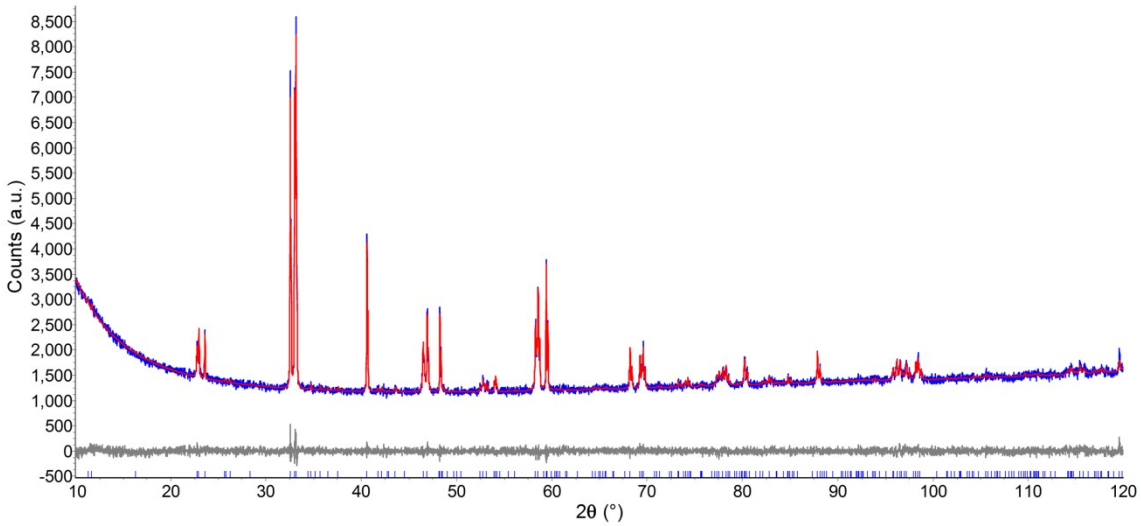

Figure S2: **Rietveld plot of the XRD data of GB9S1CO collected at room temperature (R_{wp} = 0.029, R_{Bragg} = 0.009). The observed and calculated intensity are shown by blue and red line, respectively, with the differences plotted beneath. Vertical markers indicate the Bragg reflections.**

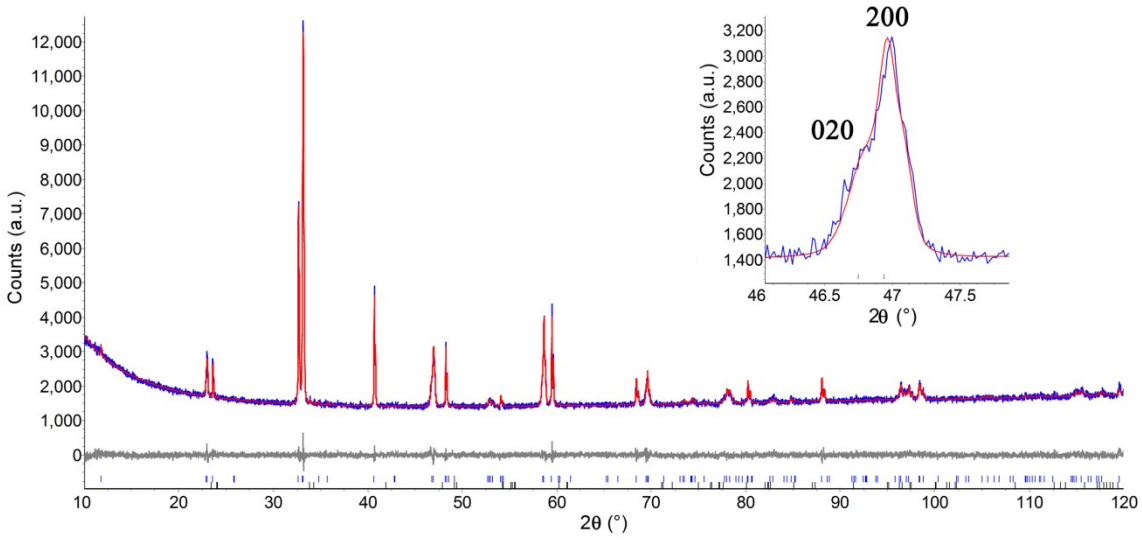

Figure S3: Rietveld plot of the XRD data of GB8S2CO collected at room temperature with the 200 and 020 region enlarged as an inset to justify the *Pmmm* space group rather than *P*4/*mmm* (R_{wp} = 0.028, R_{Bragg} = 0.005). The observed and calculated intensity are shown by blue and red line, respectively, with the differences plotted beneath. Vertical markers indicate the Bragg reflections of 99.1(2) wt.% GB8S2CO (top) and 0.9(2) wt.% $GdCoO_3$ (bottom) phases.

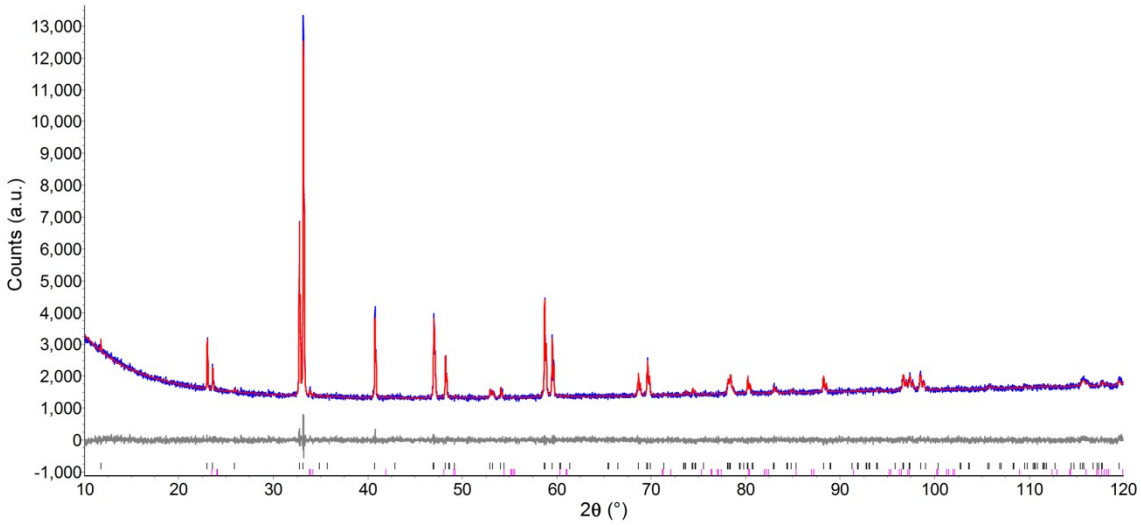

Figure S4: Rietveld plot of the XRD data of GB7S3CO collected at room temperature (R_{wp} = 0.028, R_{Bragg} = 0.006). The observed and calculated intensity are shown by blue and red line, respectively, with the differences plotted beneath. Vertical markers indicate the Bragg reflections of 98.3(3) wt.% GB7S3CO (top) and 1.7(3) wt.% $GdCoO_3$ (bottom) phases.

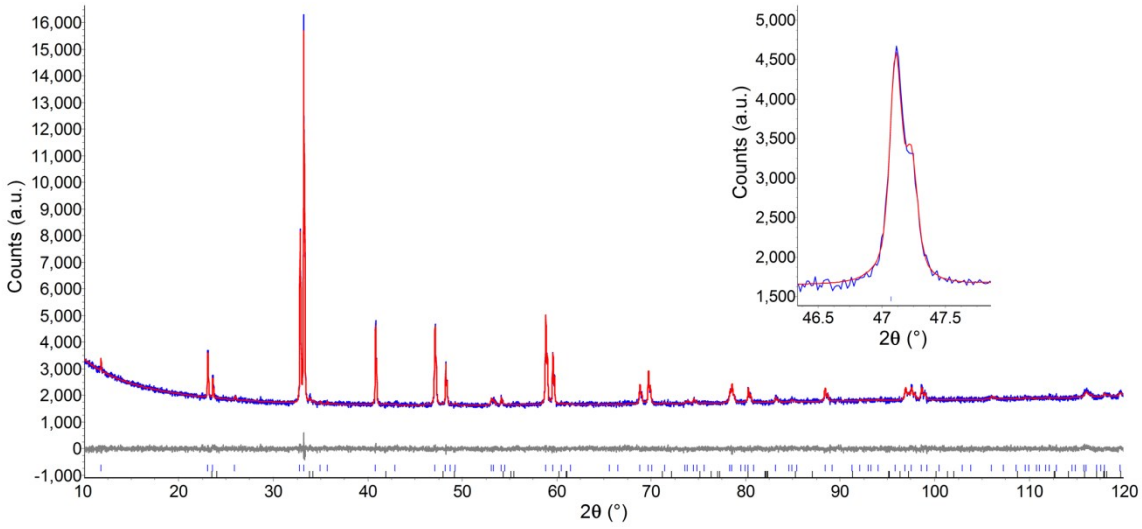

Figure S5: Rietveld plot of the XRD data of GB6S4CO collected at room temperature with the 200 region enlarged as an inset to justify the *P*4/*mmm* space group (R_{wp} = 0.025, R_{Bragg} = 0.005). The observed and calculated intensity are shown by blue and red line, respectively, with the differences plotted beneath. Vertical markers indicate the Bragg reflections of 97.6(3) wt.% GB6S4CO (top) and 2.4(3) wt.% $GdCoO_3$ (bottom) phases.

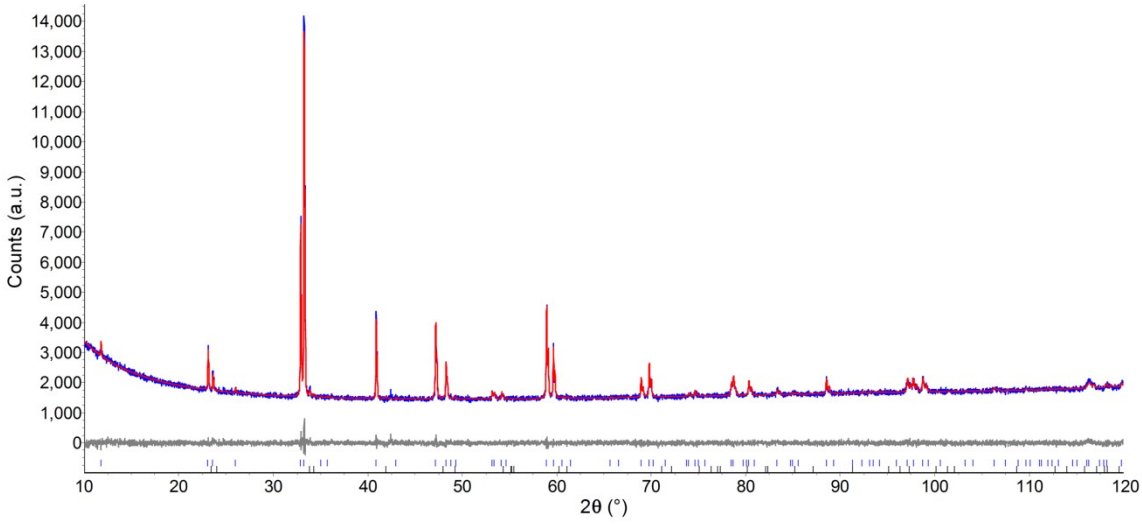

Figure S6: Rietveld plot of the XRD data of GB5S5CO collected at room temperature (R_{wp} = 0.026, R_{Bragg} = 0.004). The observed and calculated intensity are shown by blue and red line, respectively, with the differences plotted beneath. Vertical markers indicate the Bragg reflections of 97.0(3) wt.% GB6S4CO (top) and 3.0(3) wt.% $GdCoO_3$ (bottom) phases.

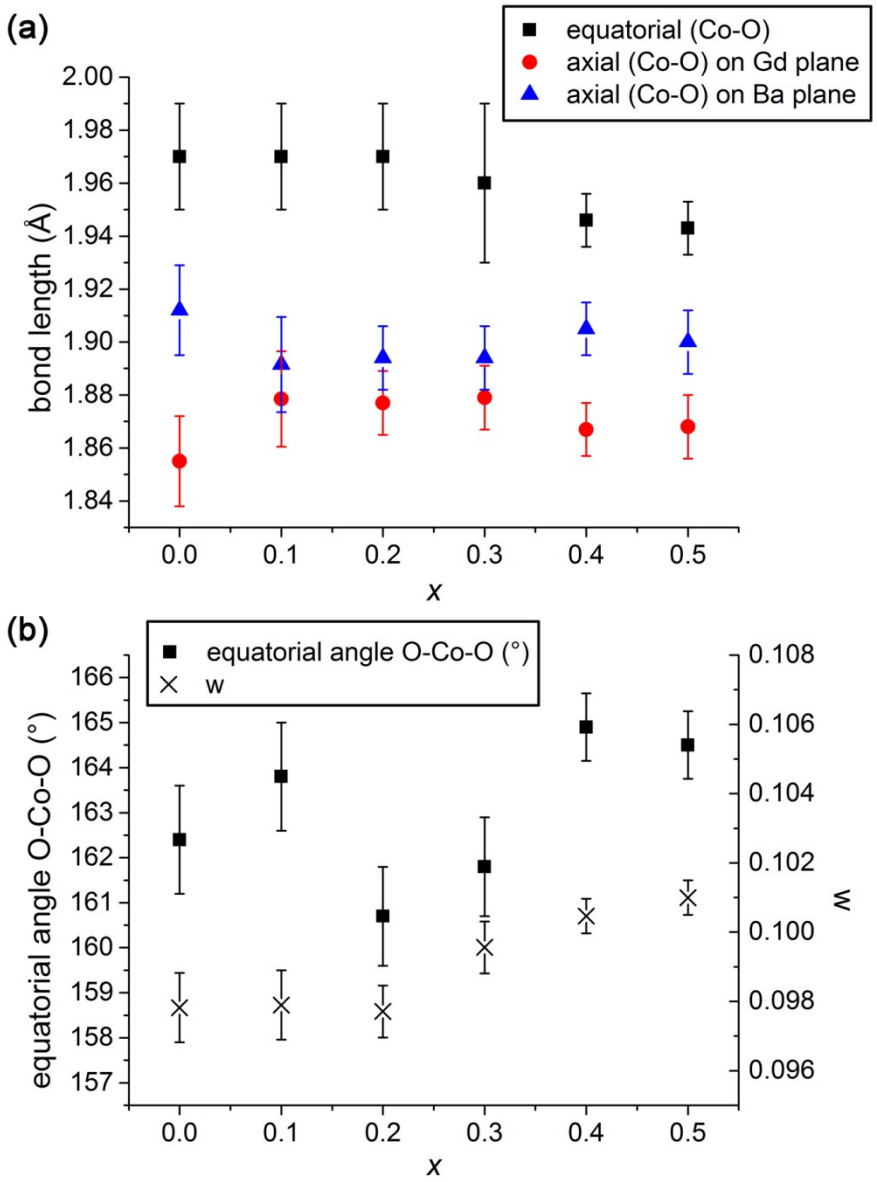

Figure S7: (a) Axial and equatorial bond lengths of Co-O and (b) equatorial buckling angle of Co-O-Co and bandwidth w.

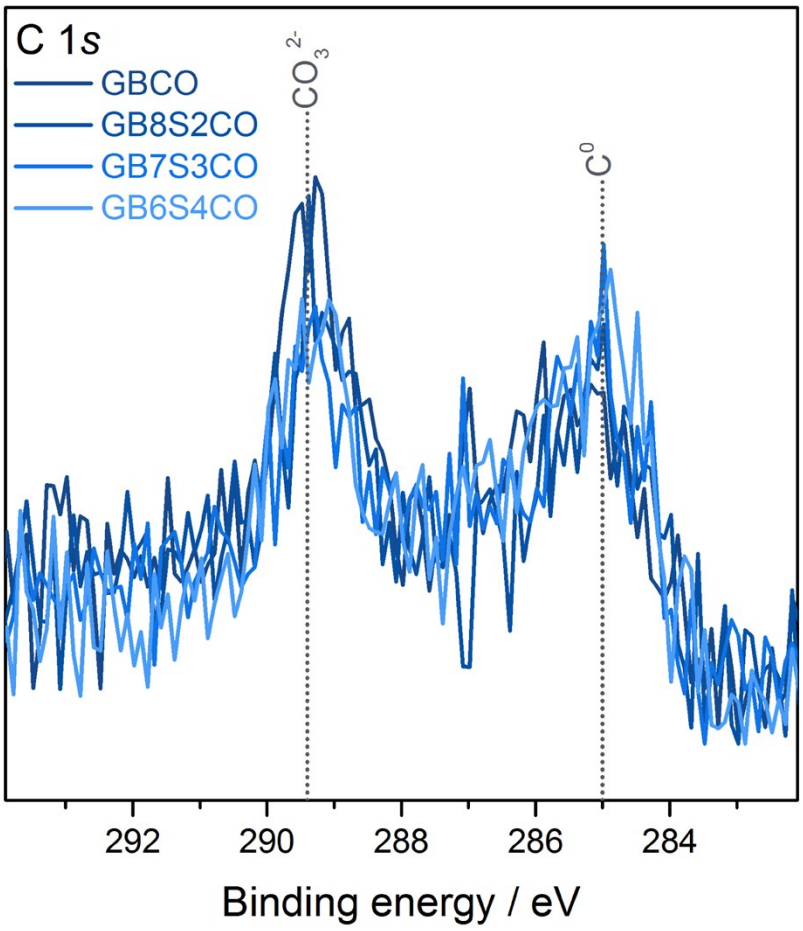

Figure S8: C 1s X-ray photoelectron spectra of GBCO, GB8S2CO, GB7S3CO, and GB6S4CO. The binding energy positions of aliphatic C^0 and carbonate CO_3^{2-} are indicated.

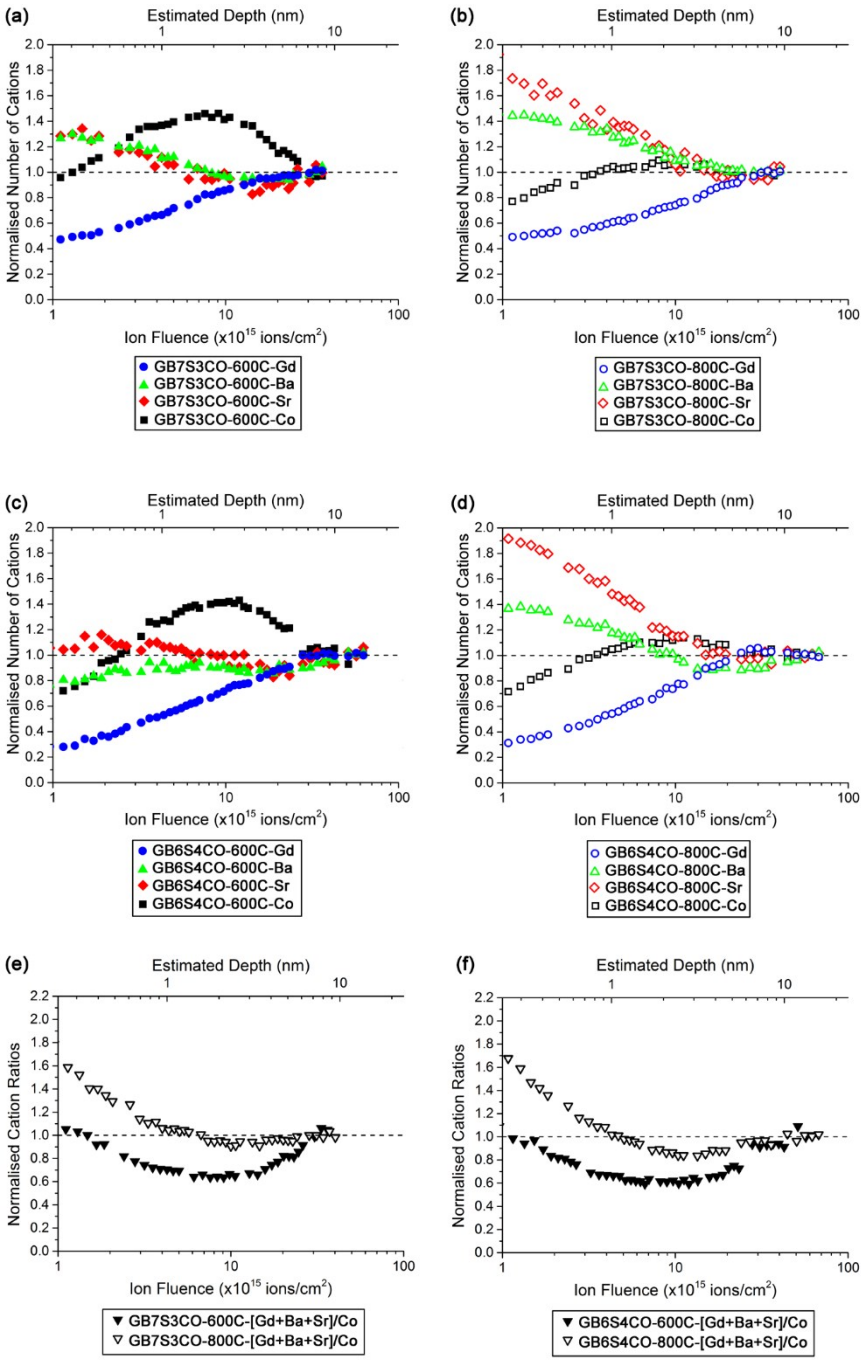

Figure S9: Cation depth profiles obtained from low energy ion scattering (LEIS) spectroscopy (a, b) individual cations in GB7S3CO annealed at 600 °C and 800 °C, respectively, (c, d) individual cations in GB6S4CO annealed at 600 °C and 800 °C, respectively, whilst (e, f) [Gd+Ba+Sr]/Co ratio in GB7S3CO and GB6S4CO, respectively.

References

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