Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

Structure, electrical conductivity and oxygen transport properties of perovskite-type oxides $CaMn_{1-x-y}Ti_xFe_yO_{3-\delta}$

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Table S1 Representative structural parameters for the phases of CMF. The numbers in parentheses denote standard deviations in units of the least significant digits.

Atom	Site	x	y	z	U_{iso}
30 °C ($\boldsymbol{Pnma}$): a = 5.2969(1) Å, b = 7.4763(2) Å, c = 5.2827(1) Å					
Ca	4c	0.0310(9)	0.25	-0.011(2)	0.002(1)
Mn,Fe	4b	0	0	0.5	0.00(3)
O1	4c	0.493(2)	0.25	0.053(3)	0.00(1)
O2	8d	0.268(4)	0.031(3)	0.692(3)	0.038(7)
800 °C ($\boldsymbol{I4/mcm}$): a = b = 5.3475(3) Å, c = 7.5609(7) Å					
Ca	4b	0	0.5	0.25	0.005(1)
Mn,Fe	4c	0	0	0	0.0(2)
O1	4a	0	0	0.25	0.00(7)
O2	8h	0.221(2)	0.721(2)	0	0.099(5)
900 °C ($\boldsymbol{Pm\bar{3}m}$): a = b = c = 3.7886(5) Å					
Ca	1a	0	0	0	0.005(1)
Mn,Fe	1b	0.5	0.5	0.5	0.0(9)
O	3d	0.5	0.5	0	0.058(2)

Note: The reliability factors for the three structural refinements are: 30 °C ($Pnma$): R_{wp} = 4.861% and χ^2 = 2.84; 800 °C ($I4/mcm$): R_{wp} = 4.529% and χ^2 = 2.07; 900 °C ($Pm\bar{3}m$): R_{wp} = 4.855% and χ^2 = 2.93.

Table S2 Representative structural parameters for the phases of CMTF. The numbers in parentheses denote standard deviations in units of the least significant digits.

Atom	Site	x	y	z	U_{iso}
30 °C ($\boldsymbol{Pnma}$): a = 5.3187(1) Å, b = 7.5062(3) Å, c = 5.3049(1) Å					
Ca	4c	0.0274(8)	0.25	-0.004(3)	0.009(1)
Mn,Fe	4b	0	0	0.5	0.00(5)
O1	4c	0.490(2)	0.25	0.066(5)	0.015(8)
O2	8d	0.285(2)	0.034(2)	0.710(3)	0.021(5)
800 °C ($\boldsymbol{I4/mcm}$): a = b = 5.3653(2) Å, c = 7.58325(4) Å					
Ca	4b	0	0.5	0.25	0.010(1)
Mn,Fe	4c	0	0	0	0.000(5)
O1	4a	0	0	0.25	0.00(1)
O2	8h	0.221(2)	0.721(2)	0	0.081(9)
900 °C ($\boldsymbol{Pm\bar{3}m}$): a = b = c = 3.7988(4)Å					
Ca	1a	0	0	0	0.003(1)
Mn,Fe	1b	0.5	0.5	0.5	0.00(2)
O	3d	0.5	0.5	0	0.058(2)

Note: The reliability factors for the three structural refinements are: 30 °C ($Pnma$): R_{wp} = 3.950 % and χ^2 = 2.23; 800 °C ($I4/mcm$): R_{wp} = 3.905% and χ^2 = 1.71; 900 °C ($Pm\bar{3}m$): R_{wp} = 4.416% and χ^2 = 2.03.

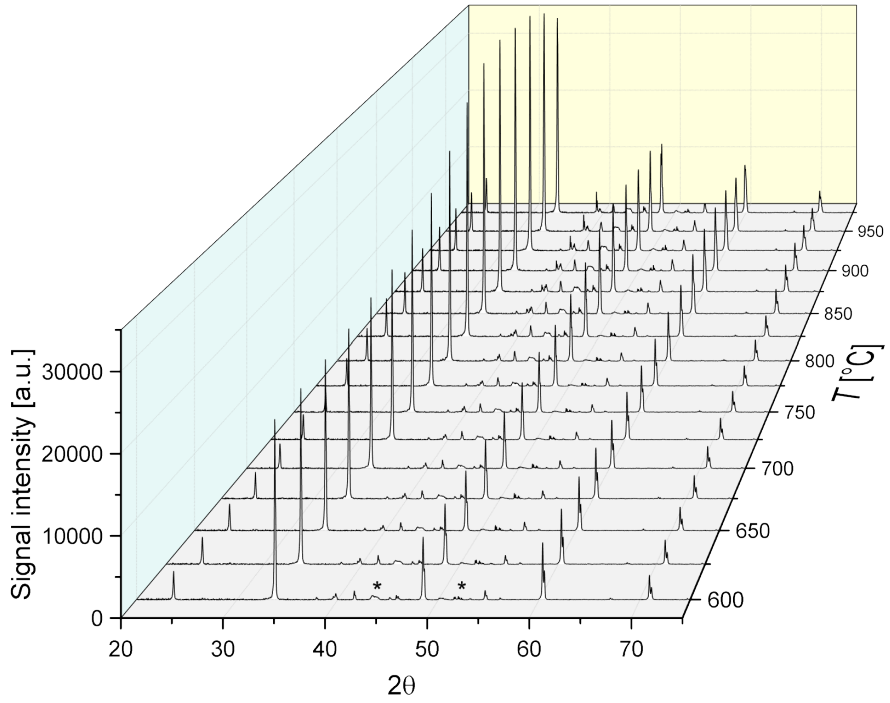

Fig. S1 HT-XRD patterns of CM recorded in air on cooling from 975 °C to 600 °C. Stars denote regions in which aberrations of the instrument are known to be present.

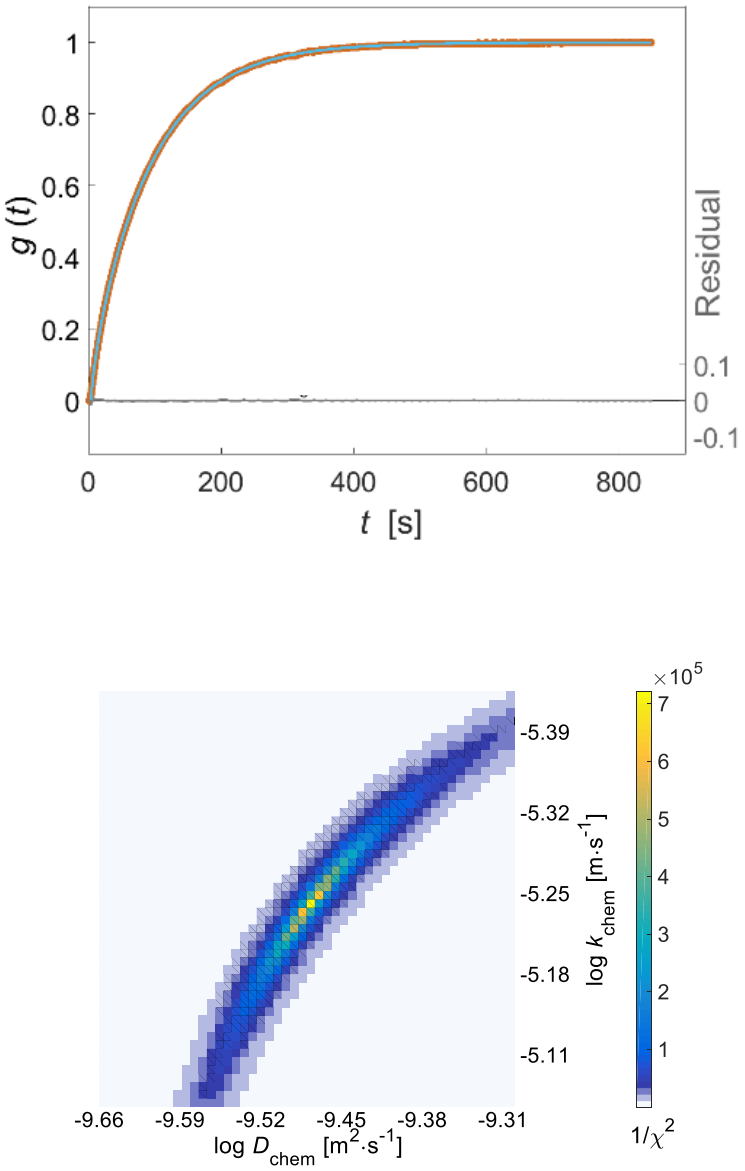

Fig. S2 (a) Normalized conductivity curve for CMF, obtained at 775 °C after a pO_2 step change from 0.146 to 0.215 atm. The solid blue line represents the non-linear least squares fit to Eqs. 2-4, and the residual is shown by the grey dots. (b) Corresponding error plot, in which the most probable values for D_{chem} and k_{chem} correspond with the highest value of $1/\chi^2$.