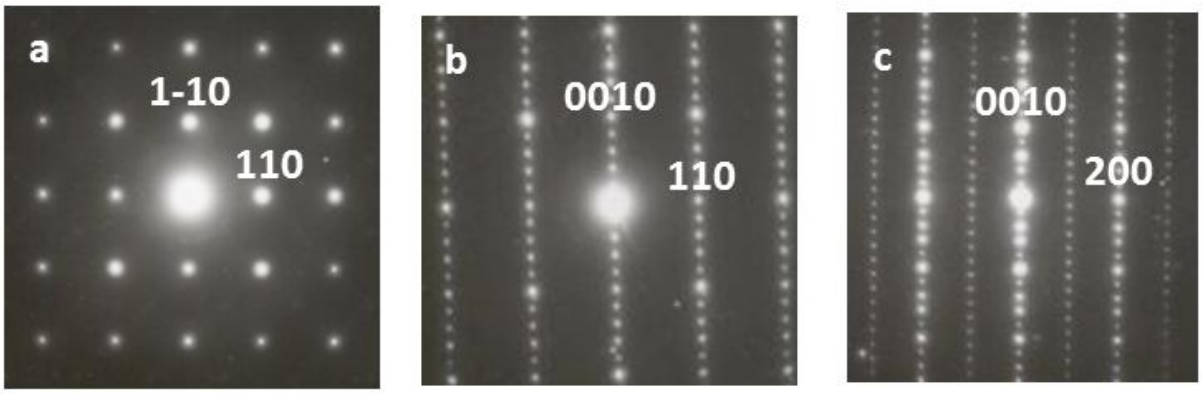
Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information



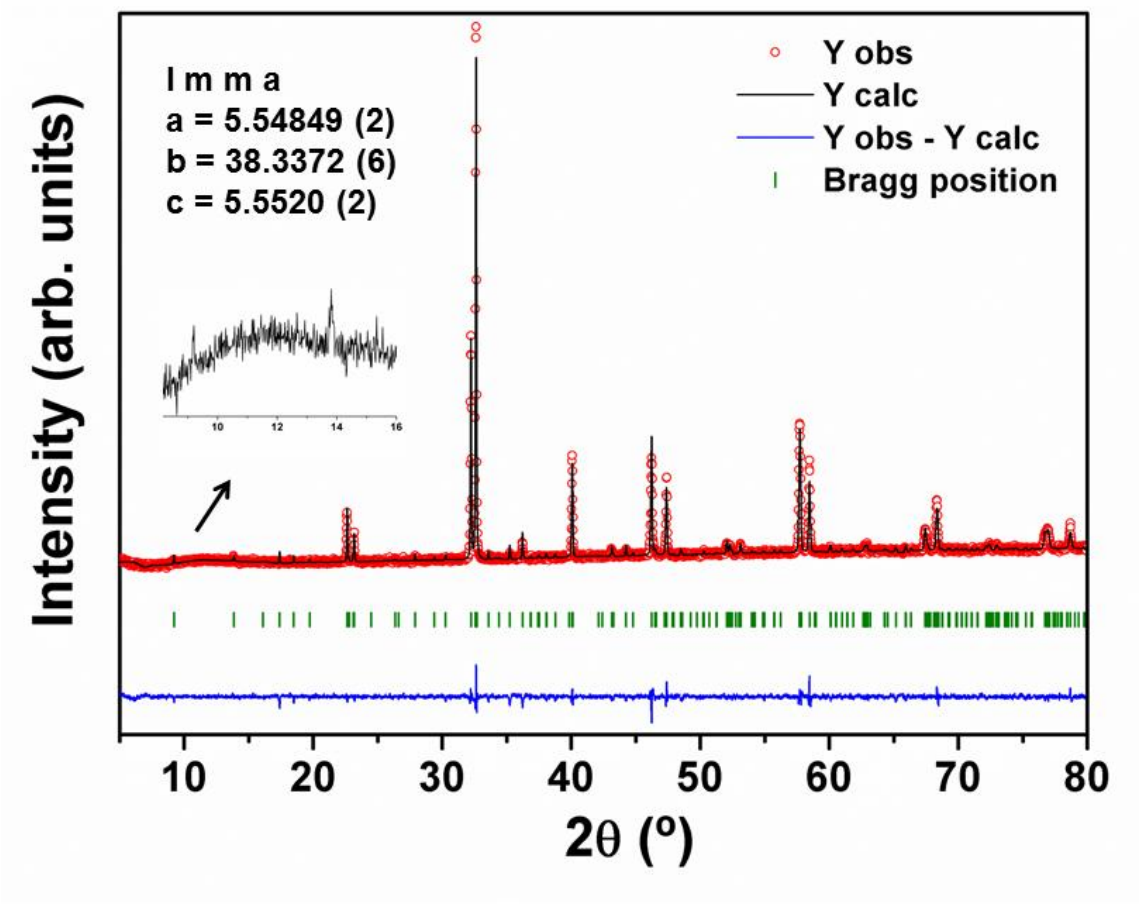


Figure S1a SAED patterns of a $(GdBa)_{0.8}Ca_{0.4}Co_{0.6}Fe_{1.4}O_{5.41}$ crystal indexed according to the 2ap × 10ap × 2ap unit cell along the (a) $[001]_p$, (b) $[010]_p$ and (c) $[-110]_p$ zone axes.

Figure S1b PXRD analysis of $(GdBa)_{0.8}Ca_{0.4}Co_{0.6}Fe_{1.4}O_{5.4}$. The experimental pattern has been collected at room temperature. The inset shows a portion of the pattern with weak superlattice reflections in agreement with a modulation of the crystal structure with $5a_p$ periodicity. Taking into account the SAED and HRTEM results, profile fitting has been carried out with Imma space group and $\sqrt{2}a_p \times 10a_p \times \sqrt{2}a_p$ unit cell. The refined unit cell parameters a = 0.554849(2) nm, b= 3.83372(6) nm and c= 0.55520(2) nm are determined. The $10a_p$ lattice parameter is set in the b axis according to the standard Imma space group.

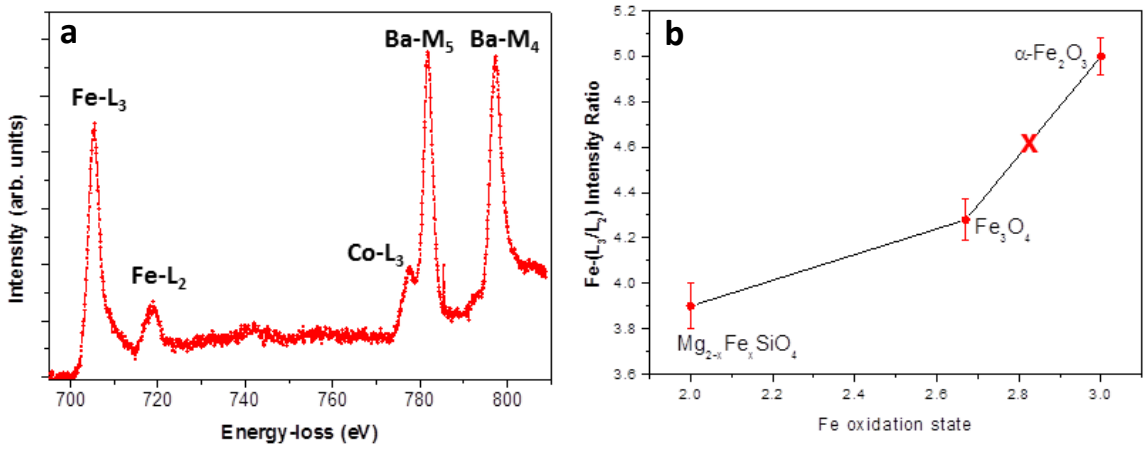


Figure S2 EELS analysis of $(GdBa)_{0.8}Ca_{0.4}Co_{0.6}Fe_{1.4}O_{6-\delta}$. a, EELS spectrum of $(GdBa)_{0.8}Ca_{0.4}Co_{0.6}Fe_{1.4}O_{6-\delta}$ showing the Fe-L_3, Fe-L_2, Co-L_3, Ba-M_5 and Ba-M_4 ionization edges. **b,** graphic representation of the L_3/L_2 intensity ratio of the Fe-$L_{2,3}$ ionization edge versus Fe oxidation state in three standard Fe compounds. The L_3/L_2 intensity ratio of the Fe-$L_{2,3}$ ionization edge of $(GdBa)_{0.8}Ca_{0.4}Co_{0.6}Fe_{1.4}O_{6-\delta}$ is indicated by a red cross.

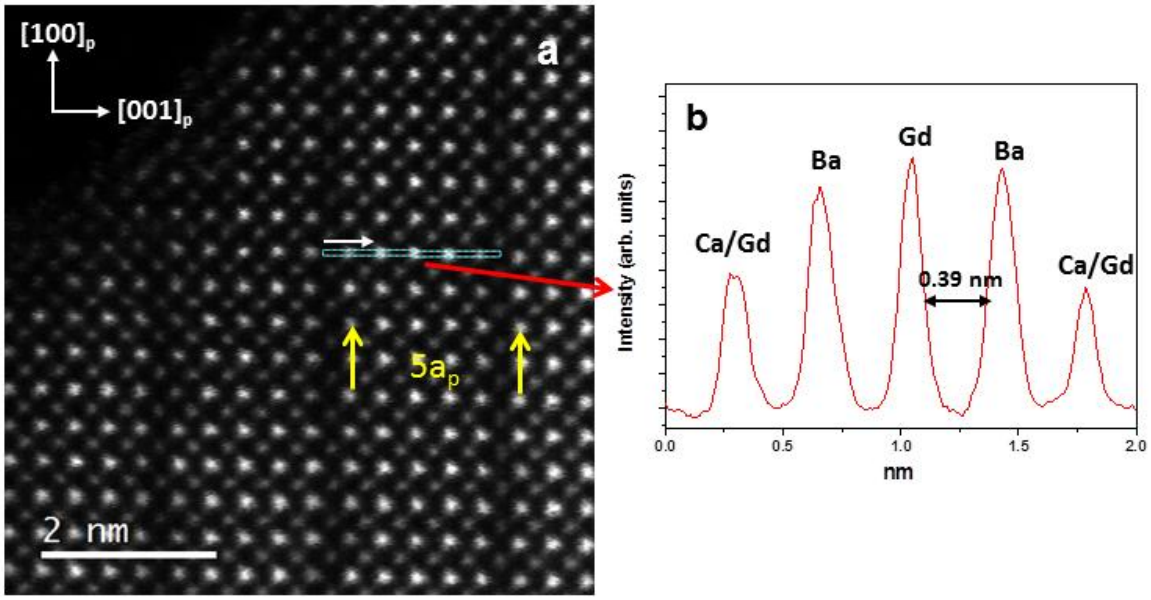


Figure S3 HAADF-STEM analysis of $(GdBa)_{0.8}Ca_{0.4}Co_{0.6}Fe_{1.4}O_{5.41}$. a, Experimental HAADF-STEM image of a crystal along the $[010]_p$ zone axis. Layered ordering of cations along the $[001]_p$ direction with $5a_p$ periodicity is indicated. **b,** Intensity line-profile along the $[001]_p$ direction collected for the columns of atoms indicated by the blue line in (a). Distance between layers (columns of A-type atoms) along the $[001]_p$ direction is 0.39 nm ($\approx a_p$). A-type atoms are Gd, Ba and Ca.

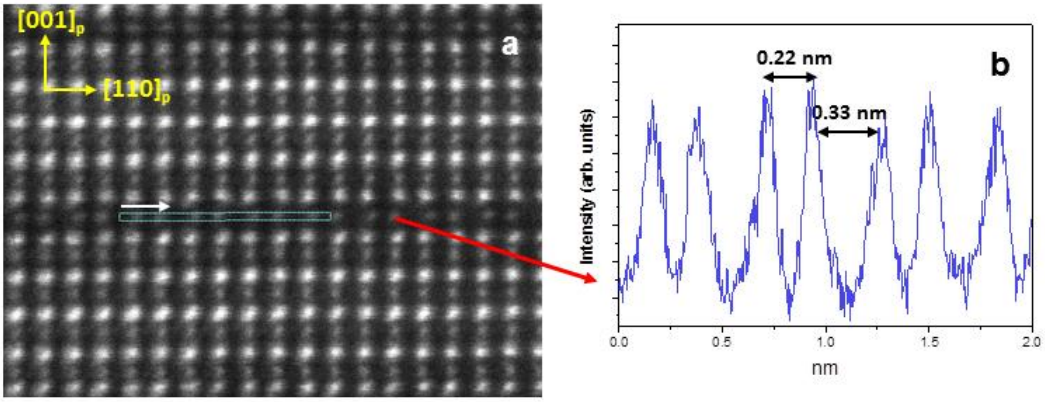


Figure S4 HAADF-STEM analysis of $(GdBa)_{0.8}Ca_{0.4}Co_{0.6}Fe_{1.4}O_{5.41}$. a, Experimental HAADF-STEM image of a crystal along the $[-110]_p$ zone axis. **b,** Intensity line-profile along the $[110]_p$ direction collected for the columns of B-type atoms (Fe and Co) indicated by the blue line in (a). Two B-B distances (0.22 and 0.33 nm) alternate along the $[110]_p$ direction. B-type atoms are Fe and Co.

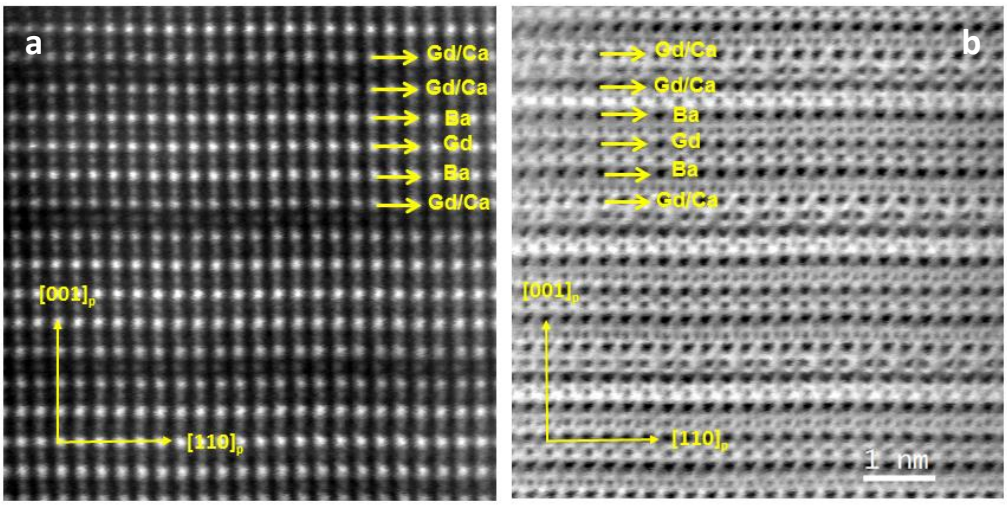


Figure S5 STEM analysis of $(GdBa)_{0.8}Ca_{0.4}Co_{0.6}Fe_{1.4}O_{5.41}$. a, Experimental HAADF-STEM image of a crystal along the $[-110]_p$ zone axis. Yellow arrows indicate cation-layers of Ca/Gd-Ba-Gd-Ba-Ca/Gd. **b,** Experimental ABF-STEM image of a crystal along the $[-110]_p$ zone axis. Yellow arrows indicate cation-layers of Ca/Gd-Ba-Gd-Ba-Ca/Gd.

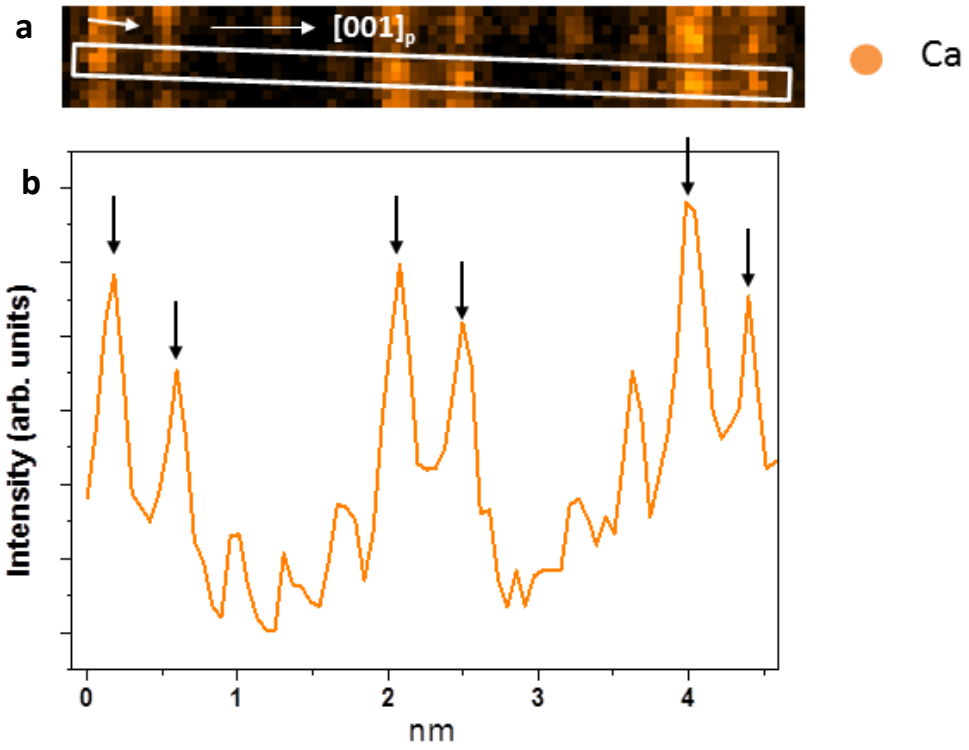


Figure S6 EELS mapping of Ca of $(GdBa)_{0.8}Ca_{0.4}Co_{0.6}Fe_{1.4}O_{5.4}$. a, The EELS map has been performed with the Ca-$L_{2,3}$ edge signals in a crystal oriented along the$[-110]_p$ zone axis. **b,** Intensity line-profile along the $[001]_p$ direction collected for the columns of Ca atoms.

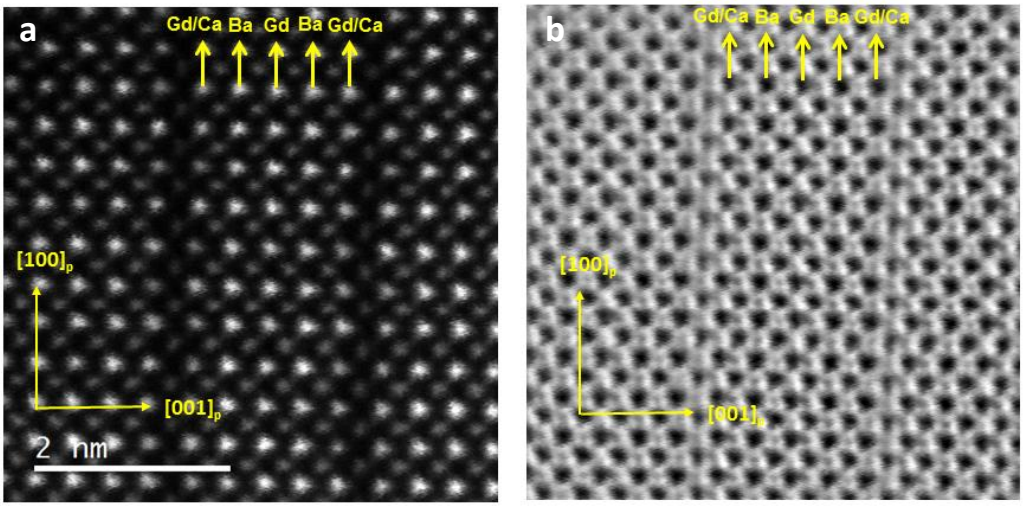


Figure S7 STEM analysis of $(GdBa)_{0.8}Ca_{0.4}Co_{0.6}Fe_{1.4}O_{5.41}$. a, Experimental HAADF-STEM image of a crystal along the $[010]_p$ zone axis. **b,** Experimental ABF-STEM image of a crystal along the $[010]_p$ zone axis. Yellow arrows indicate cation-layers of Ca/Gd-Ba-Gd-Ba-Ca/Gd.

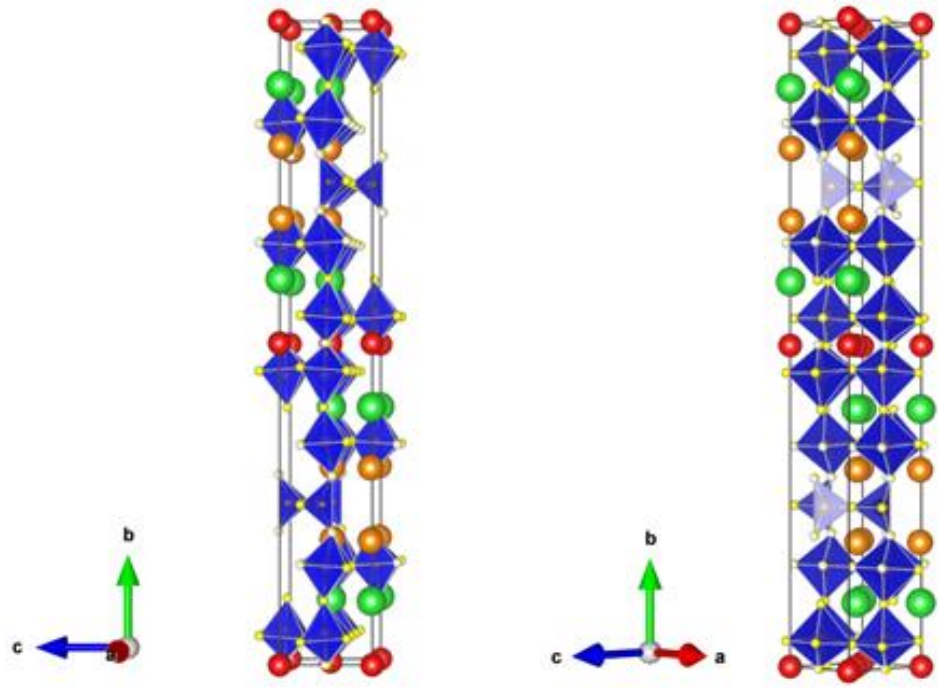


Figure S8 Ideal model of the crystal structure of $(GdBa)_{0.8}Ca_{0.4}Co_{0.6}Fe_{1.4}O_{5.4}$. Representation along $[010]_p$ (left) and $[-110]_p$ (right) build up with the measured coordinates displayed in Table 1 SI. Oxygen atoms are represented in yellow, Gd atoms are in red, Ba atoms in green and sites with both Gd and Ca atoms are indicated in orange. The coordination polyhedral around the Fe and Co atoms are represented in blue. The $10a_p$ lattice parameter is set in the b axis according to the standard Imma space group.

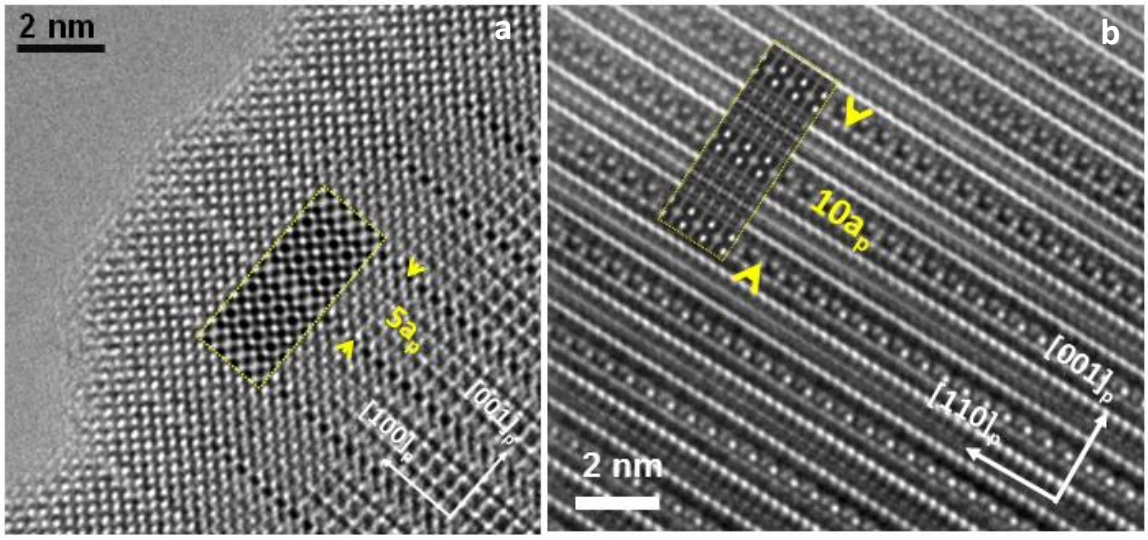


Figure S9 HRTEM image calculations of $(GdBa)_{0.8}Ca_{0.4}Co_{0.6}Fe_{1.4}O_{5.4}$. a, Experimental and calculated (Defocus Δf= -30 nm, thickness t: 2 nm) HRTEM along the $[010]_p$ zone axis. **b,** Experimental and calculated (Defocus Δf= -30 nm, thickness t: 8 nm) HRTEM along the $[-110]_p$ zone axis. The HRTEM images have been calculated HRTEM using the ideal model build up with the measured coordinates displayed in Table 1 SI and have been inserted as inset in the right part of the high-resolution image.

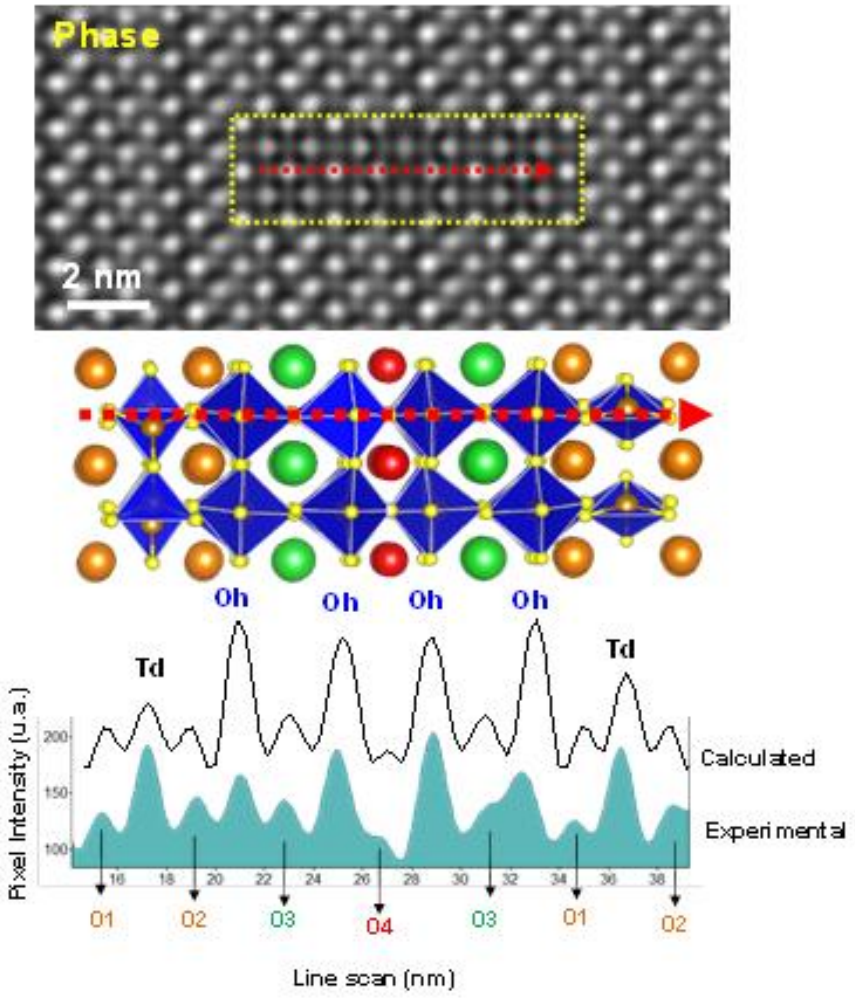


Figure S10 Comparison between the experimental image of the phase of the reconstructed exit wave of $(GdBa)_{0.8}Ca_{0.4}Co_{0.6}Fe_{1.4}O_{5.4}$ along $[010]_p$ and the simulation using the ideal model build up with the measured coordinates displayed in Table 1 SI. The dotted red arrow represents the line where the intensity profiles displayed at the bottom of the figure are measured. The same dotted arrow is also represented over the projected structural model along the $(Fe/Co)O_2$ layer sandwiched between the AO layers. The graph at the bottom compares the experimental profile with the simulated. For the simulation, the oxygen vacancies corresponding to a value of $\delta = 0.6$ are located in the crystallographic position 8h of O8 (see Table 1 SI) and nicely reproduce the lower intensity of the column named O4.

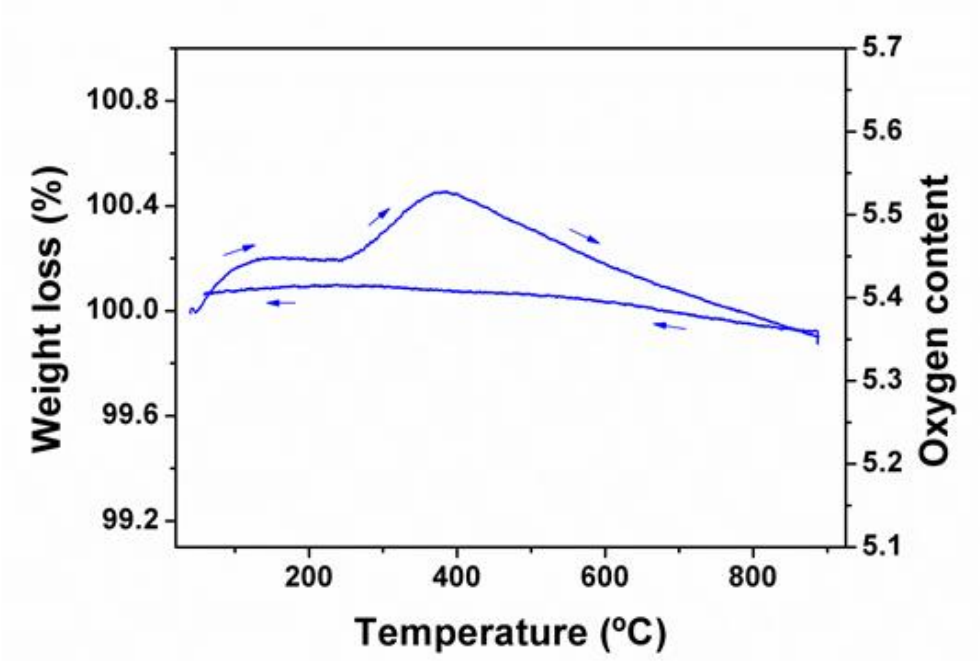


Figure S11 Thermogravimetric analysis of $(GdBa)_{0.8}Ca_{0.4}Co_{0.6}Fe_{1.4}O_{5.41}$. Thermogravimetric curves in ambient air. There is a slight increase of weight associated to oxygen gain up to 400 °C and further oxygen losses up to 800 °C. The final oxygen content after the first heating-cooling cycle is similar to the initial oxygen content of the material. The curve also shows the variation of the oxygen content with the temperature. Heating and cooling cycles are indicated by arrows.

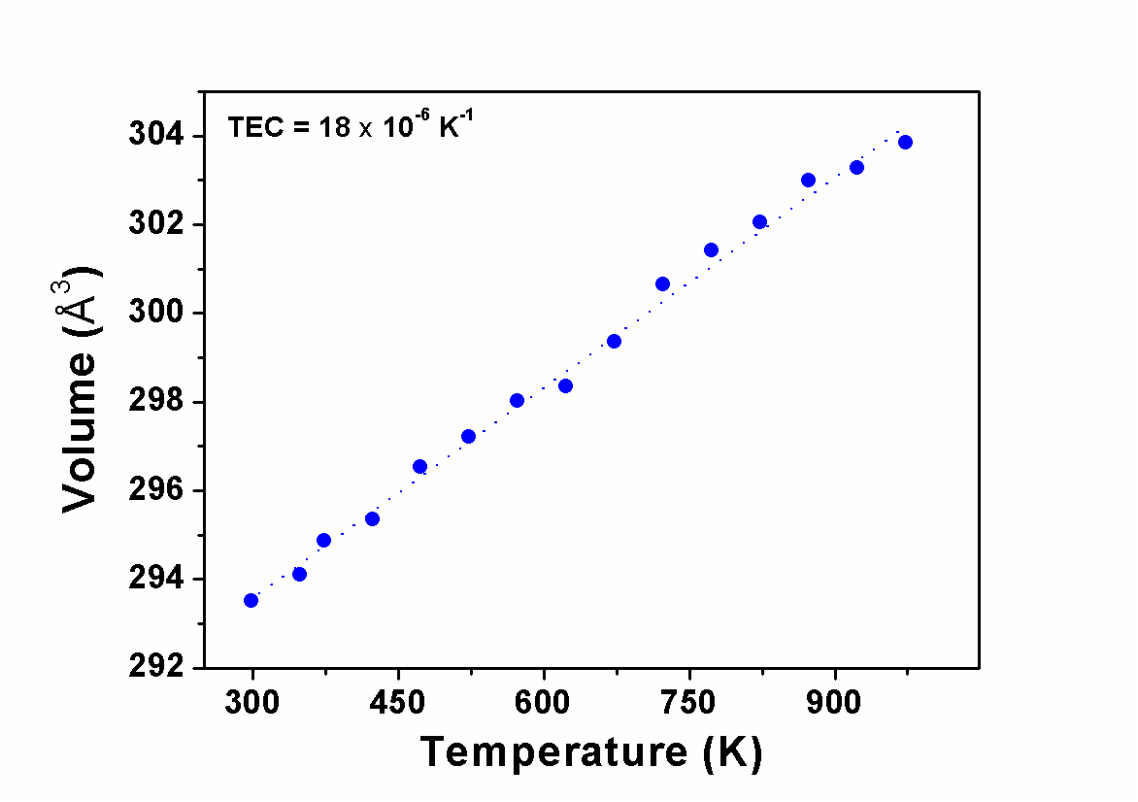


Figure S12 Volume expansion of $(GdBa)_{0.8}Ca_{0.4}Co_{0.6}Fe_{1.4}O_{5.41}$ as a function of temperature. Cell volume at each temperature has been calculated by fitting of the PXRD profile. The linear thermal expansion coefficient (αL) has been calculated as derived from the volumetric thermal expansion coefficient, αV ≡ 3αL. The value of linear thermal expansion coefficient (TEC) for $(GdBa)_{0.8}Ca_{0.4}Co_{0.6}Fe_{1.4}O_{5.41}$ is 18×10-6 K^{-1} in the temperature range from 298 to 973 K.

Atom	Wyckoff	x	y	z	Occupancy
Gd	*4a*	0.00	0.00	0.00	1
Ba	*8h*	0.00	0.56	0.99	1
Gd/Ca	*8h*	0.00	0.69	0.98	1
Fe1	*8h*	0.00	0.05	0.51	1
Fe2	*8h*	0.00	0.15	0.50	1
Fe3	*4e*	0.00	0.25	0.57	1
O1	*8g*	0.25	0.04	0.25	1
O2	*8g*	0.25	0.96	0.25	1
O3	*8g*	0.25	0.15	0.25	1
O4	*8g*	0.25	0.66	0.25	1
O5	*4d*	0.25	0.25	0.75	1
O6	*8h*	0.00	0.10	0.52	1
O7	*8h*	0.00	0.20	0.43	1
O8	*8h*	0.00	0.00	0.50	0.25

Table S1. Measured atomic coordinates in the ABF-STEM and the EWR Phase images of $(GdBa)_{0.8}Ca_{0.4}Co_{0.6}Fe_{1.4}O_{5.4}$ (S.G. Imma, a = 0.554849(2) nm, b= 3.83372(6) nm and c=0.55520(2) nm). The $10a_p$ lattice parameter is set in the b axis according to the standard Imma space group.