Supplementary Information

Figure S1 analysis of GdBaCo\textsubscript{0.7}Fe\textsubscript{1.3}O\textsubscript{5+δ} prepared in air. PXRD patterns collected at room temperature. Profile fitting has been carried out with two phases: Pmmm space group and cells $a_p \times a_p \times 2a_p$ corresponding to GdBaCo\textsubscript{0.8}Fe\textsubscript{1.2}O\textsubscript{5+δ} and Pbnm space group and cells $\sqrt{2}a_p \times \sqrt{2}b_p \times 2a_p$ corresponding to GdFeO\textsubscript{3}. Calculated patterns (black line) and their difference with experimental ones are indicated at the bottom of each panel.
Figure S2 SAED and HRTEM analysis of GdBaCo$_{1.8}$Fe$_{0.2}$O$_{5+\delta}$ prepared in air. Different patterns images along the [010]$_p$ zone axis. The patterns correspond to two different unit cells: orthorhombic $\sqrt{2}a_p \times \sqrt{2}b_p \times 2a_p$ and pseudo-tetragonal $a_p \times b_p \times 2a_p$.

Figure S3 SAED and HRTEM analysis of GdBaCo$_{1.8}$Fe$_{0.2}$O$_{5+\delta}$ prepared in argon, along the [001]$_p$ and [100]$_p$ zone axes. HRTEM image along the [100]$_p$ zone axis.
Figure S4 EELS analysis of GdBaCo$_{1.4}$Fe$_{0.6}$O$_{5+\delta}$, (a) EEL spectrum of a GdBaCo$_{1.4}$Fe$_{0.6}$O$_{5+\delta}$ crystal prepared in argon showing a typical Fe-L$_{2,3}$ edge. (b) Quantification of the average oxidation state (2.98$^+$). EELS spectra have been collected in the different oxides of the GdBaCo$_{2-x}$Fe$_x$O$_{5+\delta}$ system prepared in air or argon for determination of the average oxidation state of Fe.

Figure S5 PXRD patterns at different temperatures of GdBaCoFeO$_{5+\delta}$ prepared in argon taken from room temperature to 900 °C.
Figure S6 Arrhenius representation of the total conductivity measured in N\textsubscript{2}, air and O\textsubscript{2} atmospheres of the GdBaCoFeO\textsubscript{5+δ} prepared in argon.

Figure S7 PXRD pattern of the composite GdBaCoFeO\textsubscript{5+δ} :CGO (70 : 30 wt%) heated at 900 °C for 12 hours. The GdBaCoFeO\textsubscript{5+δ} was prepared in argon.
Figure S8 SEM image of a cross-section of a symmetrical cell GBCFO:CGO /CGO/GBCFO:CGO with GBCFO being GdBaCoFeO$_{5+δ}$ prepared in argon.