

†Electronic Supplementary Information (ESI) available:[Refined lattice parameters for  $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$  ( $x = 0\text{-}0.6$ ) and variable temperature XRD data obtained for  $\text{PrBaCo}_2\text{O}_{6-\delta}$  at  $p\text{O}_2=10^{-4}$  atm]. See DOI: 10.1039/c4dt00847b/

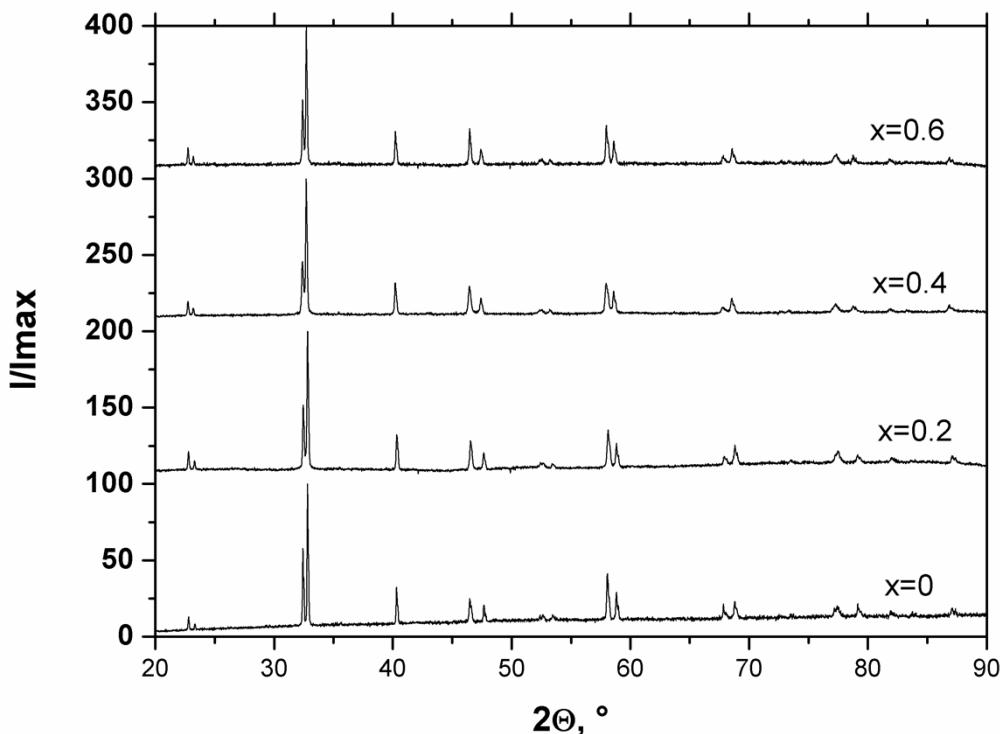


Fig. S1. XRD patterns of slowly (~100 °C/hour) cooled double perovskites of nominal compositions  $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$  ( $x = 0\text{-}0.6$ ).

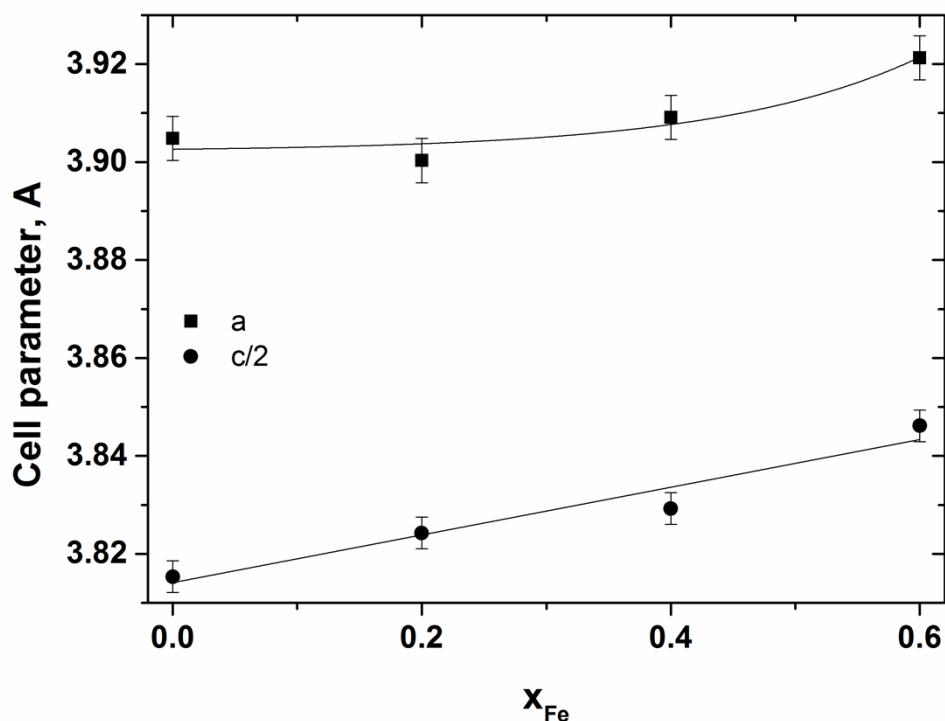


Fig. S2. Lattice parameters of  $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$  ( $x = 0\text{-}0.6$ ) as a function of Fe content at room temperature. Lines are guide to eye only.

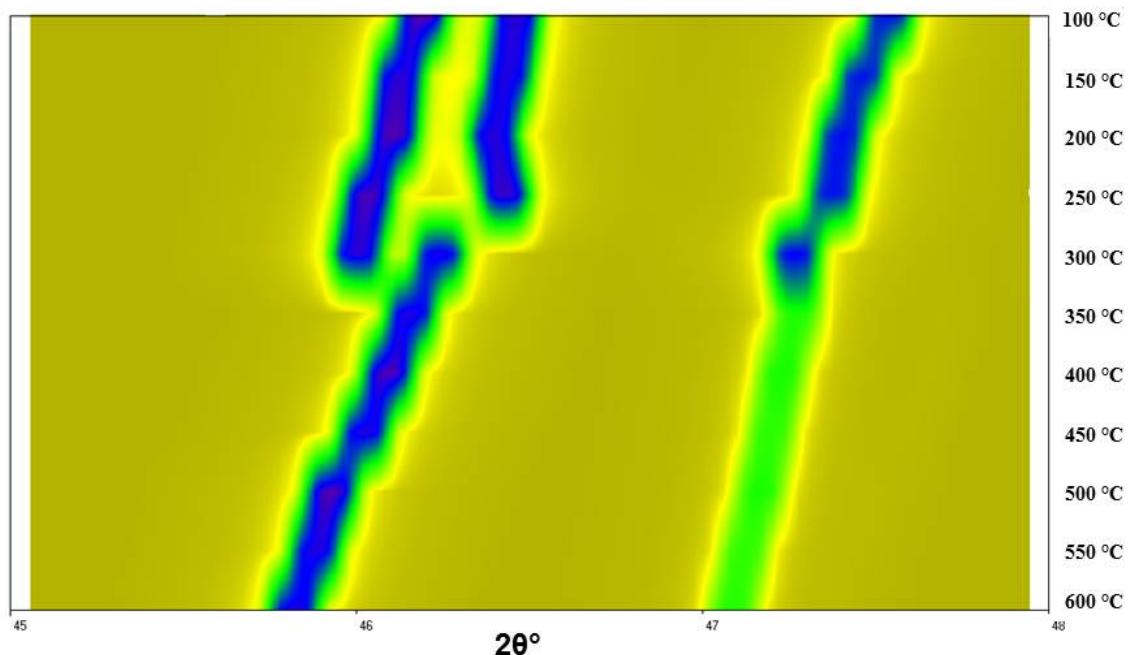


Fig. S3. Variable temperature XRD data in  $2\theta$  range  $45\text{-}48^\circ$  for  $\text{PrBaCo}_{2}\text{O}_{6-\delta}$  at  $p\text{O}_2=10^{-4}$  atm.

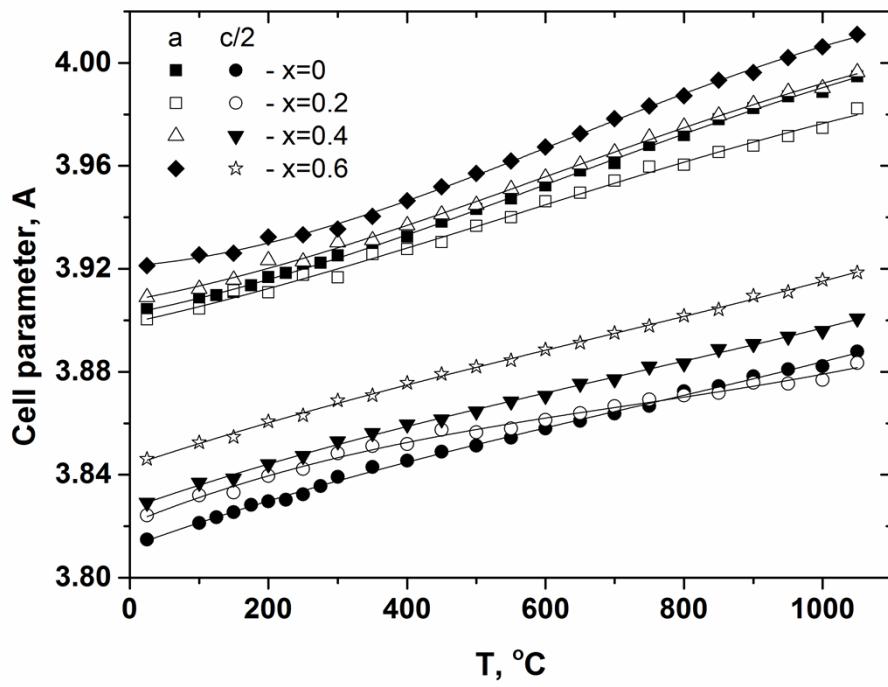


Fig. S4. Lattice parameters of  $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$  ( $x = 0-0.6$ ) vs. temperature in air. Symbols are experimental data and lines are guide to eye.

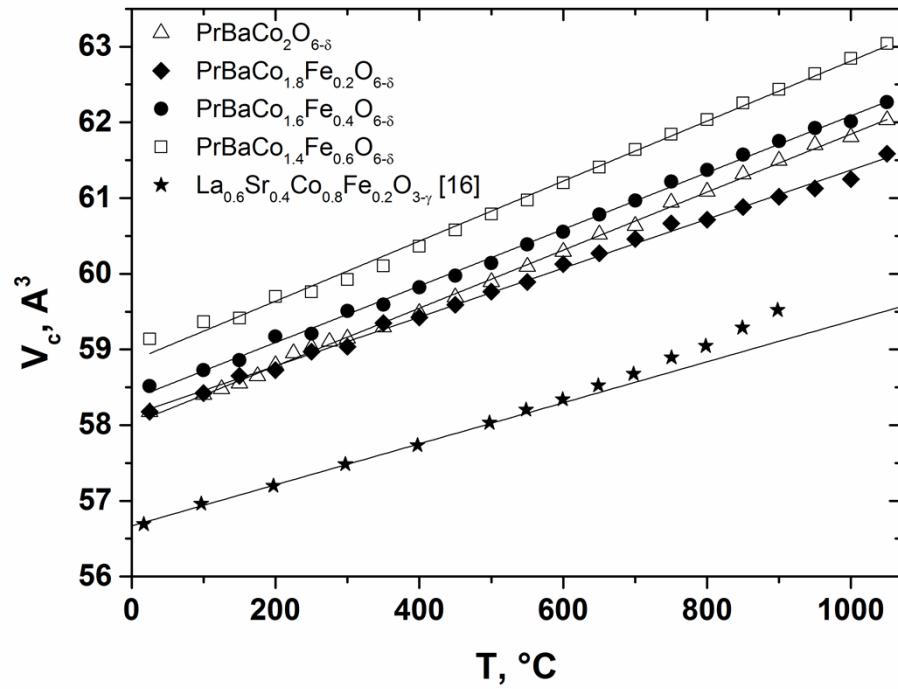


Fig. 5. Cell volumes of  $\text{PrBaCo}_{2-x}\text{Fe}_x\text{O}_{6-\delta}$  ( $x = 0-0.6$ ) and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\gamma}^{16}$  vs. temperature in air. Lines are linear fit results.