## Supporting Information

## Table of Contents

S1) Powder X-ray diffraction data of the $\mathrm{BaYCo}_{2} \mathrm{O}_{5+\delta}$ sample. The calculated pattern, shown in red, is the pattern calculated from the Rietveld refinement. The experimental pattern is shown in blue. Miller indices are shown for the primary tetragonal perovskite phase. Unassigned peaks belong to a cubic perovskite phase and $\mathrm{Y}_{2} \mathrm{O}_{3}$.

S2) Powder X-ray diffraction data of the $\mathrm{BaLaCo}_{2} \mathrm{O}_{5+\delta}$ sample. The calculated pattern, shown in red, is the pattern calculated from the Rietveld refinement. The experimental pattern is shown in blue. Miller indices are shown for the primary cubic perovskite phase (black) and the La-rich phase related to $\mathrm{La}_{4} \mathrm{Co}_{3} \mathrm{O}_{9}$ (blue).

S3) Powder X-ray diffraction data of the $\mathrm{BaYFe}_{2} \mathrm{O}_{5+\delta}$ sample. The calculated pattern, shown in red, is the pattern calculated from the Rietveld refinement. The experimental pattern is shown in blue. Miller indices are shown for the tetragonal perovskite phase. Unassigned peaks belong to $\mathrm{YFeO}_{3}$ and $\mathrm{BaFe}_{2} \mathrm{O}_{4}$.

S4) Table of structural parameters for the target perovskite phases.

S1)


S2)


S3)


S4)

| Phase | Space Group | Refined Lattice Parameters |
| :---: | :---: | :---: |
| BaLaFe ${ }_{2} \mathrm{O}_{5+\delta}$ | P/4mmm | $\begin{aligned} & a=3.931 \AA \\ & b=3.931 \AA \\ & c=7.849 \AA \\ & \alpha=90^{\circ} \\ & \beta=90^{\circ} \\ & \gamma=90^{\circ} \end{aligned}$ |
| $\mathrm{Ba}_{2} \mathrm{LaFe}_{3} \mathrm{O}_{7+\delta}$ | Pm-3m | $\begin{aligned} & a=3.993 \AA \\ & b=3.993 \AA \\ & c=3.993 \AA \\ & \alpha=90^{\circ} \\ & \beta=90^{\circ} \\ & \gamma=90^{\circ} \end{aligned}$ |
| $\mathrm{BaYCo}_{2} \mathrm{O}_{5+\delta}$ | $\mathrm{P} / 4 \mathrm{mmm}$ | $\begin{aligned} & a=3.871 \AA \\ & b=3.871 \AA \\ & c=7.495 \AA \\ & \alpha=90^{\circ} \\ & \beta=90^{\circ} \\ & \gamma=90^{\circ} \end{aligned}$ |
| $\mathrm{BaLaCo}_{2} \mathrm{O}_{5+\delta}$ | Pm-3m | $\begin{aligned} & a=3.881 \AA \\ & b=3.881 \AA \\ & c=3.881 \AA \\ & \alpha=90^{\circ} \\ & \beta=90^{\circ} \\ & \gamma=90^{\circ} \end{aligned}$ |
| $\mathrm{BaYFe}_{2} \mathrm{O}_{5+\delta}$ | $\mathrm{P} / 4 \mathrm{mmm}$ | $\begin{aligned} & a=3.924 \AA \\ & b=3.924 \AA \\ & c=7.825 \AA \\ & \alpha=90^{\circ} \\ & \beta=90^{\circ} \\ & \gamma=90^{\circ} \end{aligned}$ |

