

1 Supplemental information for

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3 **Atomic-scale determination of cation and**
4 **magnetic order in the triple perovskite**

5 **Sr₃Fe₂ReO₉**

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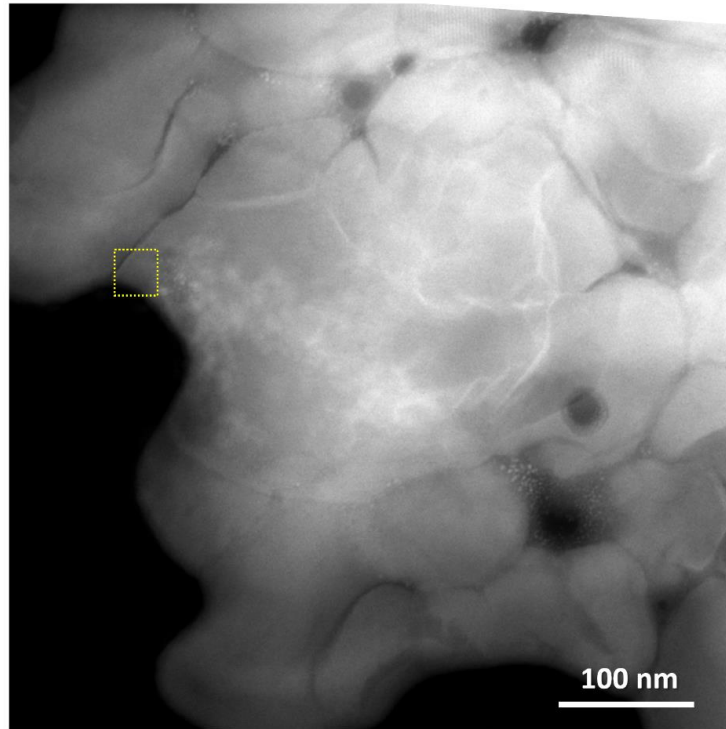
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44 Figure S1. High-angle annular dark-field scanning transmission electron microscopy
45 (HAADF STEM) image showing a small fraction of the $\text{Sr}_3\text{Fe}_2\text{ReO}_9$ phase in the
46 $\text{Sr}_2\text{Fe}_{1+x}\text{Re}_{1-x}\text{O}_6$ sample with Re deficiency. The yellow dashed square marks the
47 position of the high-magnification HAADF STEM image shown in Figure 1a.

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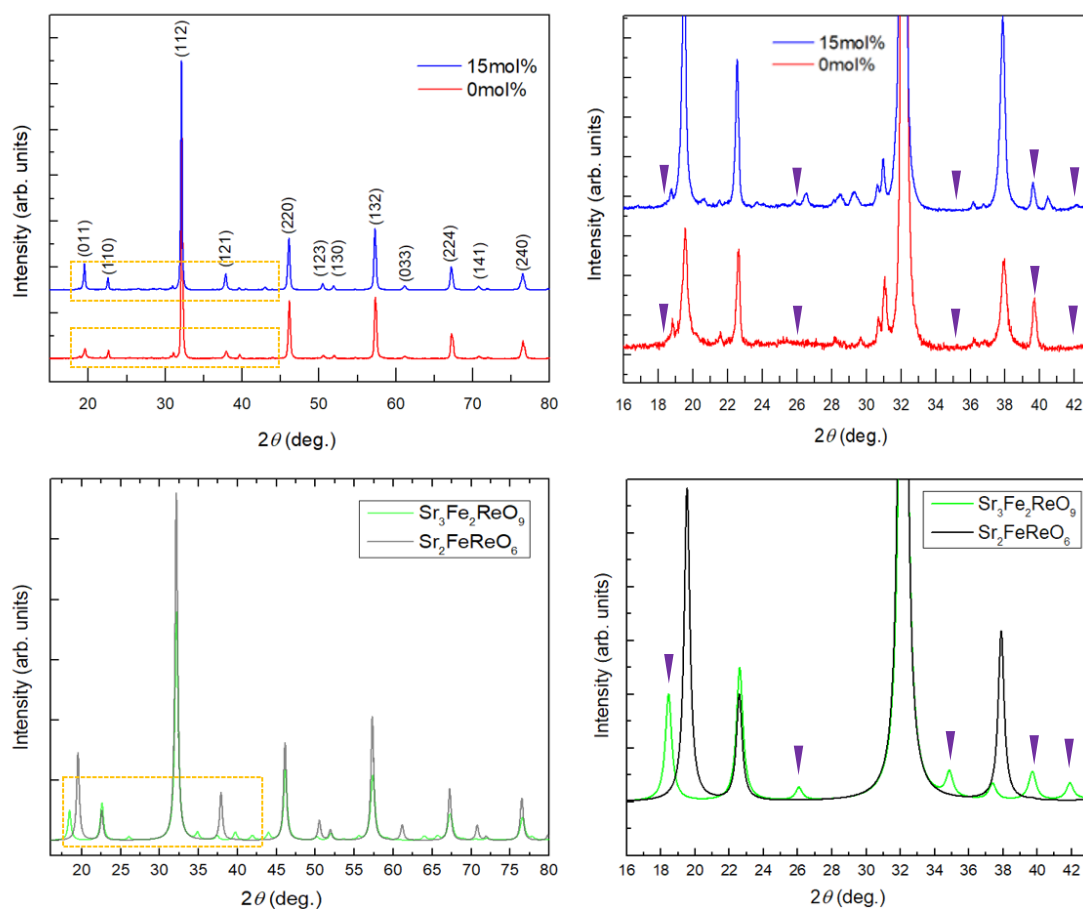
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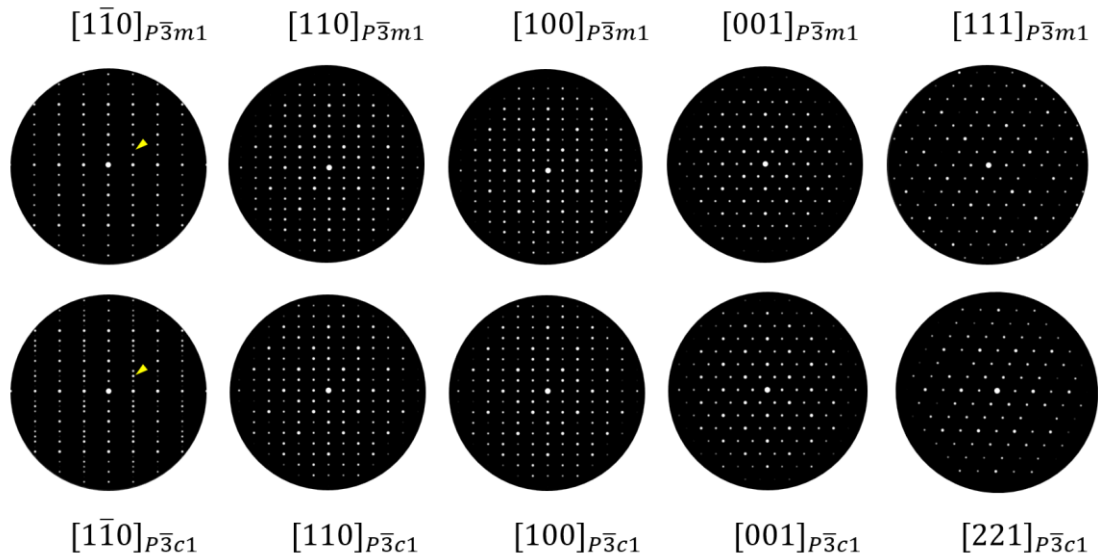
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62 Figure S2. (a) Full-range and (b) magnified X-ray powder diffraction (XRD) patterns
 63 of powders of the perovskite oxide Sr₂FeReO₆ (blue) with 15 mol% Re excess and
 64 Sr₂Fe_{1+x}Re_{1-x}O₆ (red) with 0 mol% Re excess. (c) Full-range and (d) magnified
 65 simulated XRD patterns of the 1:2 B-site-ordered triple perovskite
 66 Sr₃[Fe]_{B₁}[Fe]_{B₂}[Re]_{B₃}O₉ (light green) and the rock-salt-ordered double perovskite
 67 Sr₂[Fe]_{B₁}[Re]_{B₂}O₆ (solid black). Purple arrows indicate the theoretical positions of the
 68 characteristic diffraction peaks of the 1:2 B-site-ordered triple perovskite Sr₃Fe₂ReO₉
 69 phase, which cannot be observed in experimental XRD patterns of a Sr₂Fe_{1+x}Re_{1-x}O₆
 70 bulk sample, as shown in Figure S2b.

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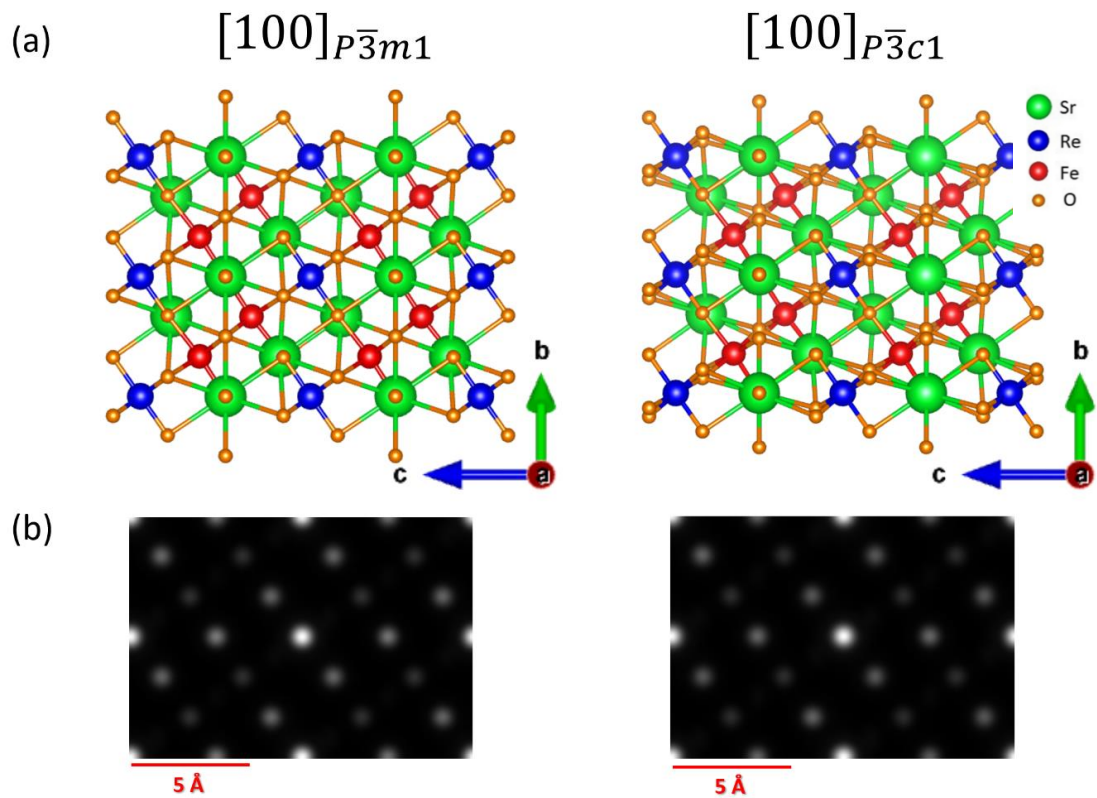
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Figure S3. Simulated electron diffraction patterns of 1:2 B-site-ordered $\text{Sr}_3\text{Fe}_2\text{ReO}_9$ with space group $P\bar{3}m1$ along $[1\bar{1}0]$, $[110]$, $[100]$, $[001]$ and $[111]$, compared with space group $P\bar{3}c1$ along $[1\bar{1}0]$, $[110]$, $[100]$, $[001]$ and $[221]$. (Note that $[221]_{P\bar{3}c1}$ corresponds to $[111]_{P\bar{3}m1}$). Super-reflection spots are indicated by yellow arrows.



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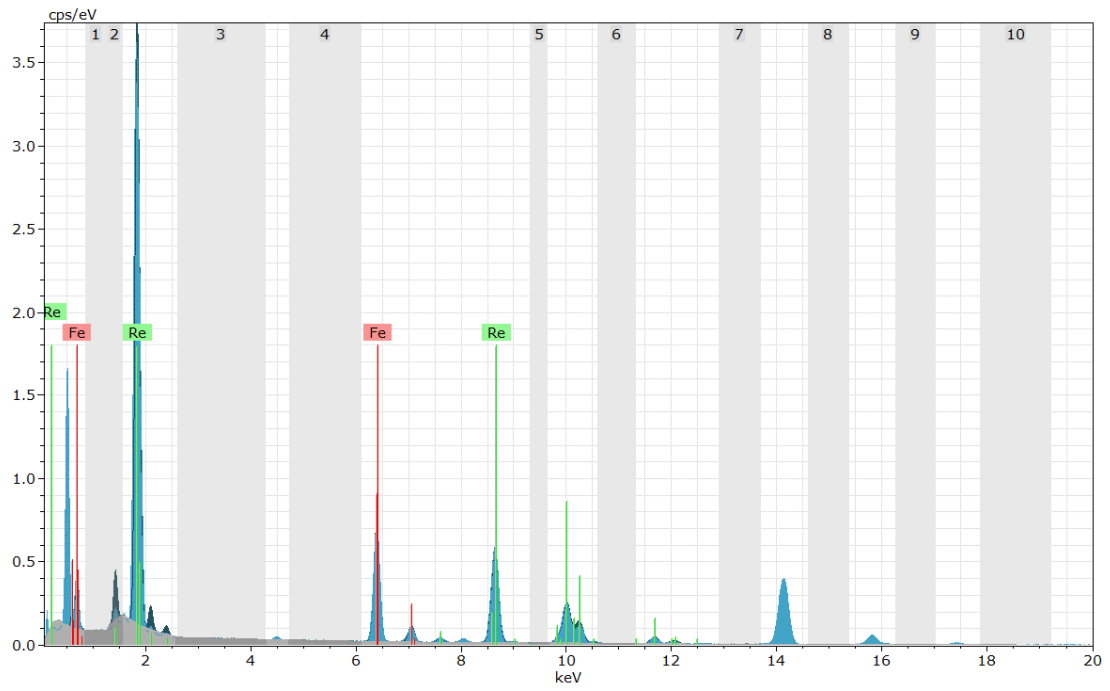
100 Figure S4. (a) Crystal structures with Sr in green, Fe in red, O in orange and Re in blue,
 101 and (b) simulated high-angle annular dark-field scanning transmission electron
 102 microscopy images of the 1:2 B-site-ordered triple perovskite $\text{Sr}_3\text{Fe}_2\text{ReO}_9$ with space
 103 groups $P\bar{3}m1$ and $P\bar{3}c1$.

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Figure S5. Energy-dispersive X-ray spectrum of $\text{Sr}_3\text{Fe}_2\text{ReO}_9$.

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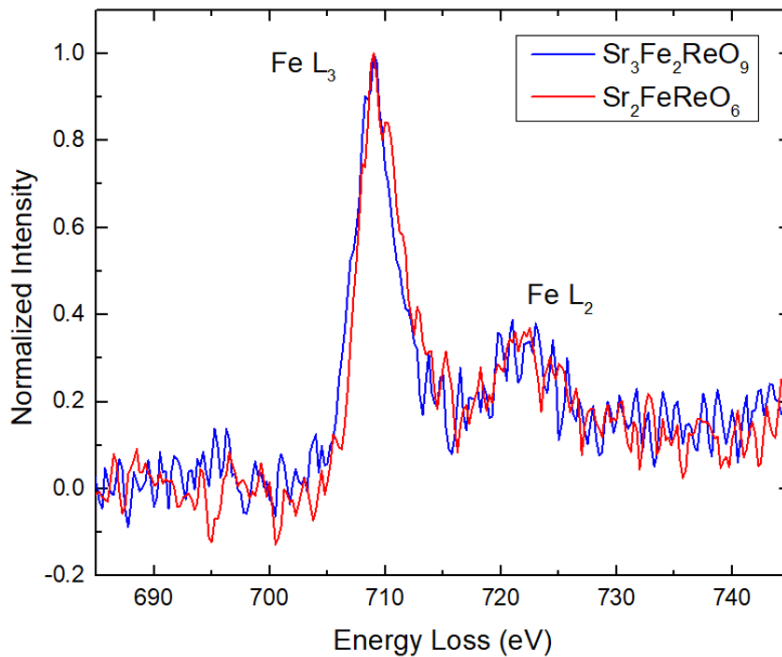
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120 Figure S6. Electron energy-loss near-edge fine structures of the Fe $L_{2,3}$ -edges recorded
 121 from the 1:2 B-site-ordered triple perovskite $\text{Sr}_3\text{Fe}_2\text{ReO}_9$ (blue) and 1:1 B-site-ordered
 122 double perovskite $\text{Sr}_2\text{FeReO}_6$ (red).

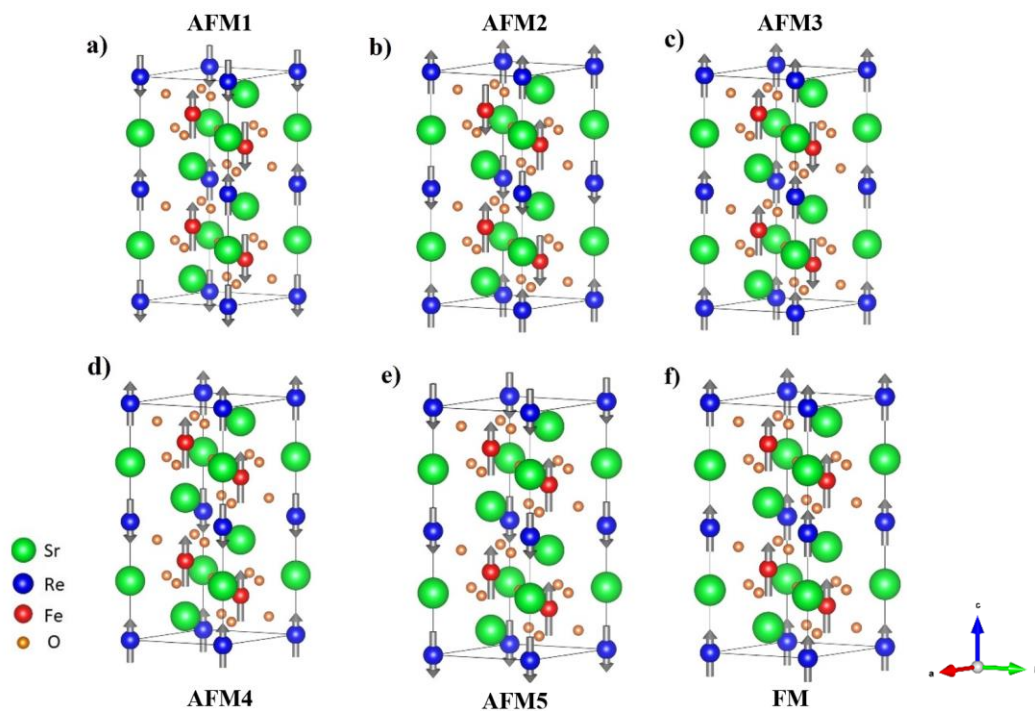
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124 Electron energy-loss spectroscopy (EELS) under nanobeam illumination
 125 conditions was performed at 300 kV in an FEI Themis 60-300 microscope equipped
 126 with a double spherical aberration corrector with a STEM spatial resolution of ~ 59 pm.
 127 A Gatan Quantum spectrometer provided an energy resolution of ~ 0.9 eV with an EELS
 128 semi-collection angle of ~ 2.5 mrad. Data processing of EEL spectra included pre-edge
 129 background subtraction, removal of plural scattering by Fourier-ratio deconvolution
 130 and normalization by integration of the post-edge intensity. The sample thickness was
 131 determined from low-loss EEL spectra.

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136 Figure S7. Magnetic configuration states of the 1:2 B-site-ordered triple perovskite
 137 $\text{Sr}_3\text{Fe}_2\text{ReO}_9$: (a) AFM1; (b) AFM2; (c) AFM3; (d) AFM4; (e) AFM5; (f) FM.

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