Supporting Information

$(Sr_{1-x}Ba_x)FeO_2$ ($0.4 \leq x \leq 1$): A New Oxygen-Deficient Perovskite Structure

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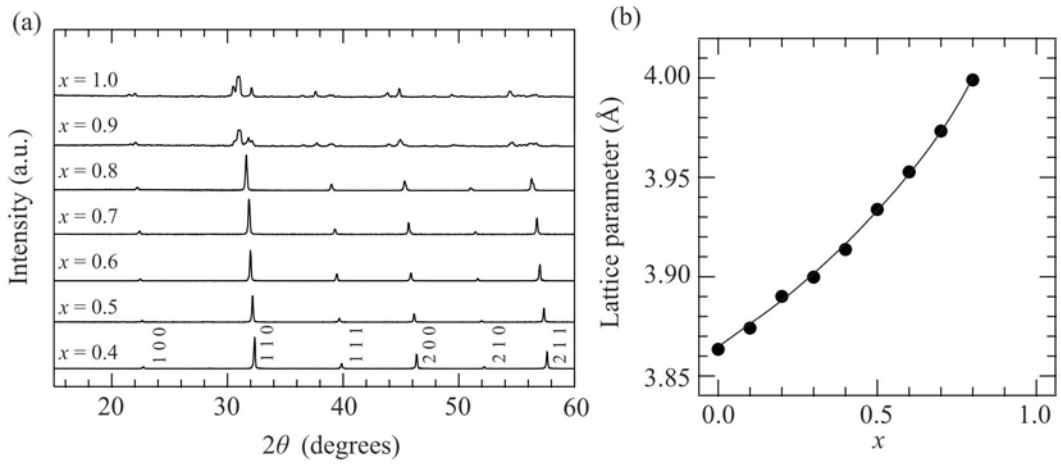

Figure 1S. (a) XRD patterns of the precursors before reduction. The patterns for x = 0.4, 0.5, 0.6, 0.7, and 0.8 could be assigned as cubic perovskite $(Sr_{1-x}Ba_x)FeO_{3-\delta}$ ($\delta < 0.5$), and those for x = 0.9 and 1.0 could be assigned as $(Sr_{1-x}Ba_x)FeO_{2.5}$ with a monoclinic $BaFeO_{2.5}$ structure.[33] (b) Lattice parameters of $(Sr_{1-x}Ba_x)FeO_{3-\delta}$ ($0 \le x \le 0.8$). The lattice parameters for x = 0.0 – 0.3 were those obtained from previous studies.[26,29] The solid line is a guide to the eye. The XRD patterns for x = 0.9 and 1.0 are readily indexed on the basis of a monoclinic unit cell with lattice parameters a = 6.978(4) Å, b = 11.015(7) Å, c = 23.117(16) Å, β = 98.22(4)°, V = 1758.6(19) Å^3 for x = 0.9 and a = 6.950(1) Å, b = 11.555(2) Å, c = 23.567(3) Å, β = 97.53(1)°, V = 1876.3(5) Å^3 for x = 1.0.

Table 1S. Tetragonal lattice parameters for $(Sr_{1-x}Ba_x)FeO_2$ obtained by least square method.

x	a (Å)	c (Å)
0[a]	3.99107(3)	3.47481(5)
0.1[a]	3.9977(10)	3.5114(13)
0.2[a]	4.0007(7)	3.5442(13)
0.3[a]	4.0089(7)	3.5835(9)
0.4	4.0779(11)	3.7869(32)
0.5	4.1045(5)	3.8067(17)
0.6	4.1143(7)	3.8226(24)
0.7	4.1319(5)	3.8370(18)
0.8	4.1499(6)	3.8473(19)
0.9	4.1725(17)	3.8631(17)
1.0	4.1873(7)	3.8787(7)

[a] We used the values for $x = 0.0 - 0.3$ in previous studies.[26,29] For $0.4 \leq x \leq 1.0$, the normalized lattice parameters are used.

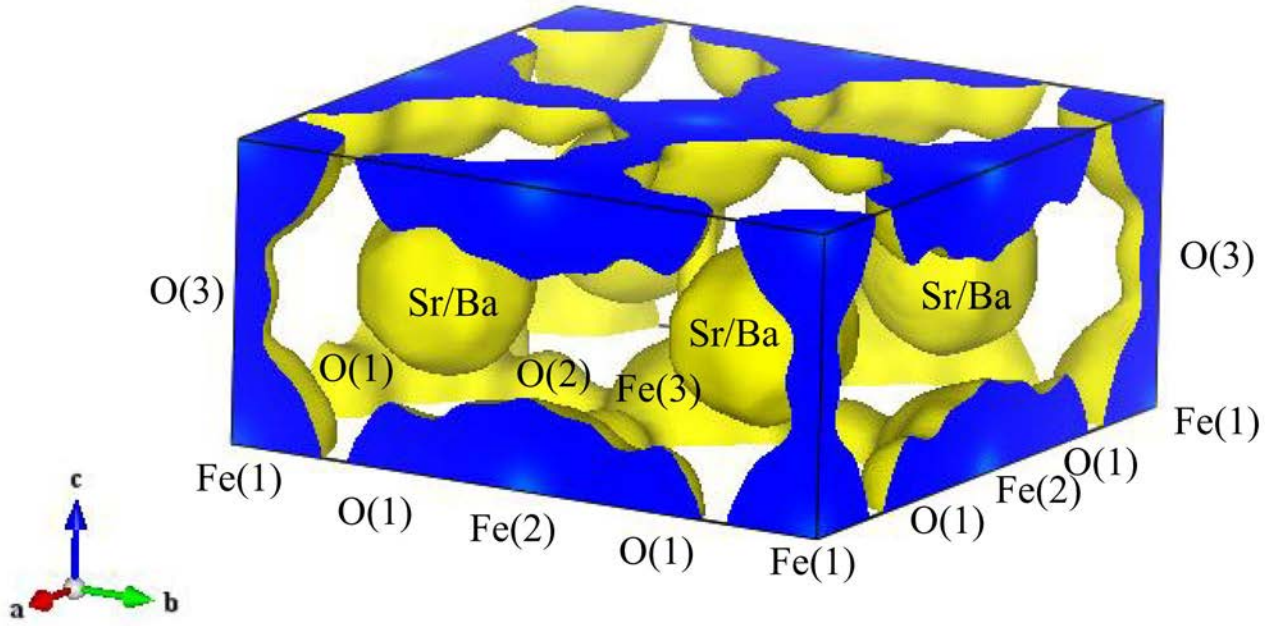

Figure 2S. Electron density map by maximum entropy method (MEM) analysis, showing electron density at the apical sites.

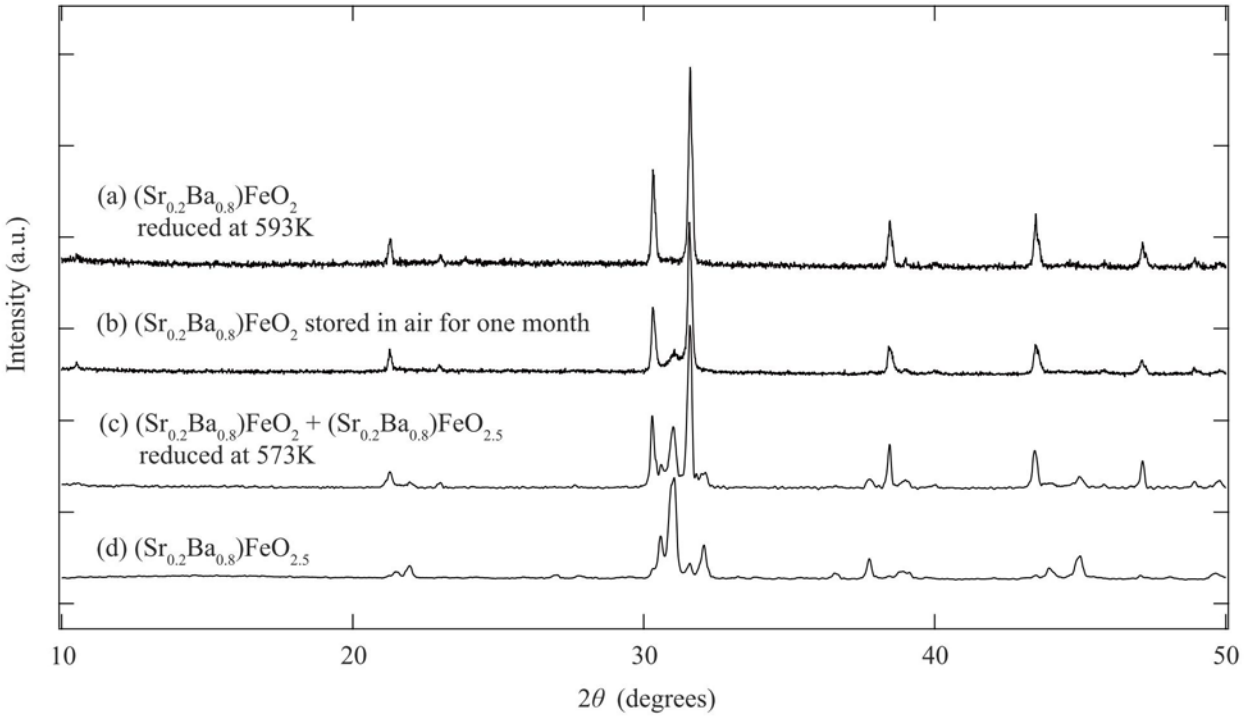

Figure 3S. XRD patterns for the x = 0.8 samples in various conditions: (a) obtained by a reaction at 593 K for 3 days, (b) obtained by a reaction at 593 K for 3 days after storage in air for one month, (c) obtained by a reaction at 573 K for 3 days, and (d) $(Sr_{0.2}Ba_{0.8})FeO_{2.5}$. The data of (a) and (b) were obtained using a D8 ADVANCE diffractometer (Bruker AXS), and those of (c) and (d) using a M18XHF diffractometer (Mac Science). In (c) and (d), peaks from Cu $K_{\alpha 2}$ radiation are removed.

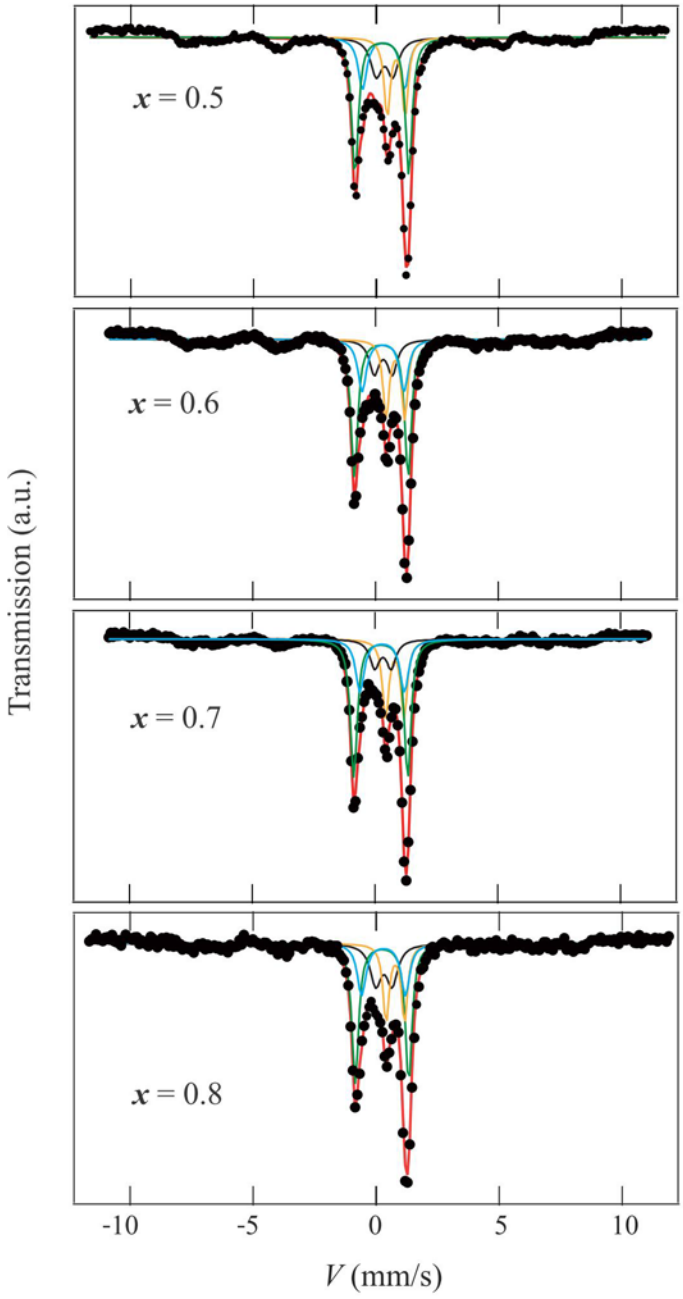

Figure 4S. Mössbauer spectra for x = 0.5, 0.6, 0.7, and 0.8 at room temperature. Circles denote the experimental data. The spectrum was fitted by four parameters; yellow, green, and blue lines represent spectra from Fe(1), Fe(2), Fe(3), respectively. The black line represents an overreduced, decomposed impurity formed during the hydride reaction. The red line represents the total of the four components.

Table 2S. Fitting parameters of Mössbauer spectra for $(Sr_{1-x}Ba_x)FeO_2$ (x= 0.5, 0.6, 0.7, 0.8).

Fe(1)

x	*IS* (mm/s)	*HF* (T)	*QS* (mm/s)	FWHM (mm/s)	Area (%)
0.5	0.806	0.0	0.74	0.30	21.2
0.6	0.810	0.0	0.76	0.30	22.0
0.7	0.809	0.0	0.75	0.31	22.6
0.8	0.784	0.0	0.76	0.30	22.8

Fe(2)

x	*IS* (mm/s)	*HF* (T)	*QS* (mm/s)	FWHM (mm/s)	Area (%)
0.5	0.229	0.0	2.19	0.33	41.2
0.6	0.233	0.0	2.19	0.33	42.6
0.7	0.234	0.0	2.20	0.33	43.9
0.8	0.247	0.0	2.21	0.37	41.5

Fe(3)

x	*IS* (mm/s)	*HF* (T)	*QS* (mm/s)	FWHM (mm/s)	Area (%)
0.5	0.296	0.0	1.71	0.42	19.7
0.6	0.306	0.0	1.70	0.42	20.4
0.7	0.291	0.0	1.81	0.42	21.0
0.8	0.285	0.0	1.76	0.42	21.0

Impurity

x	*IS* (mm/s)	*HF* (T)	*QS* (mm/s)	FWHM (mm/s)	Area (%)
0.5	0.335	0.0	0.67	0.55	17.9
0.6	0.316	0.0	0.73	0.48	15.1
0.7	0.324	0.0	0.67	0.48	12.5
0.8	0.370	0.0	0.68	0.48	14.7

[a] *IS*, *HF*, *QS*, FWHM and Area represent isomer shift, hyperfine field, quadrupole splitting, full width at half maximum and area percentage of total fit, respectively.

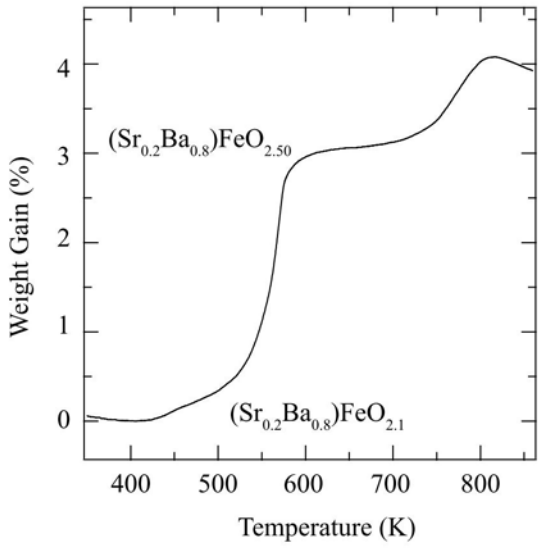

Figure 5S. Oxidation behavior of $(Sr_{0.2}Ba_{0.8})FeO_2$ (x = 0.8) under a flow of oxygen. The sample was used for the Mössbauer measurement in Figure 6, which is the different from that used for the TG measurement in Figure 3. The initial decrease of the mass at 400 K corresponds to release of moisture. When the impurity was ignored, the oxygen content was calculated to be 2.1. This is consistent with the existence of the Fe(III) impurity phase, which can be found in the Mössbauer measurement (Figure 6).

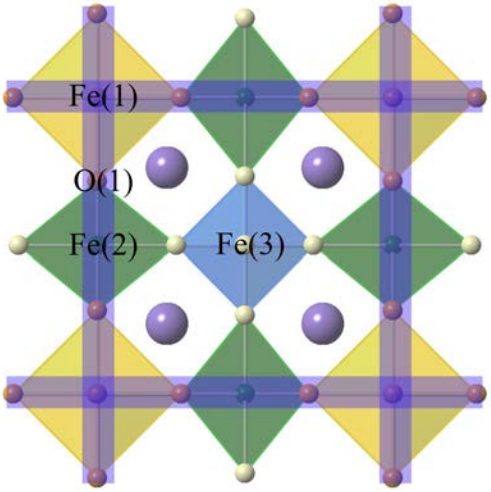

Figure 6S. The [001] projection of the $BaFeO_2$ structure, where the blue band highlights the in-plane Fe-O-Fe connections free from oxygen deficiency.

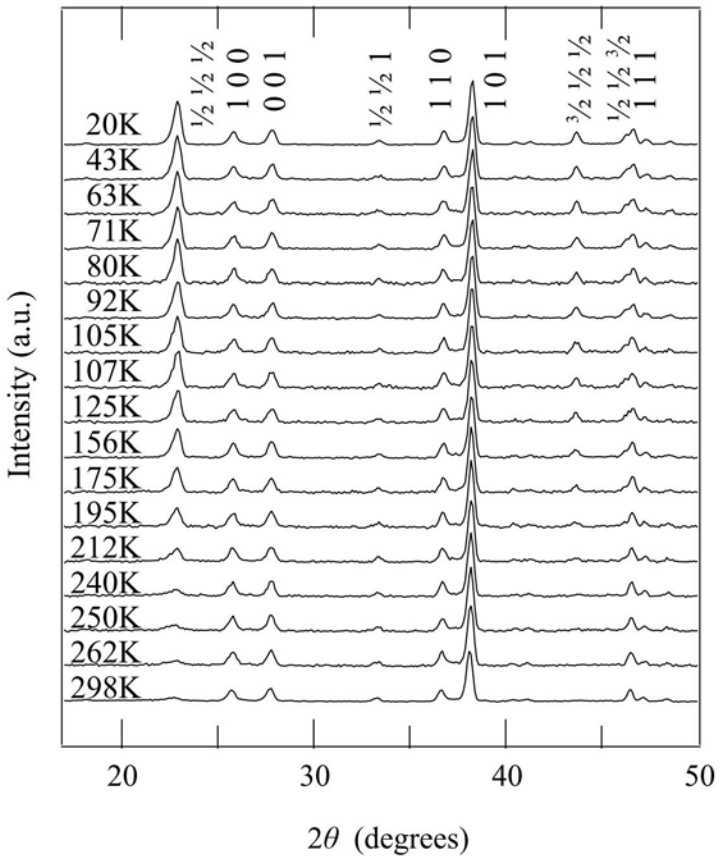

Figure 7S. Temperature dependence of neutron diffraction patterns for $x = 0.6$.

Table 3S. Fitting parameters of Mössbauer spectra for $(Ba_{0.8}La_{0.2})FeO_{2+\delta}$.

Fe(1)

x	*IS* (mm/s)	*HF* (T)	*QS* (mm/s)	FWHM (mm/s)	Area (%)
Fe(1)	0.762	0.0	0.85	0.30	21.7
Fe(2)	0.282	0.0	2.25	0.36	40.8
Fe(3)	0.332	0.0	1.44	0.45	19.9
impurity	0.324	0.0	0.67	0.48	18. 6

[a] *IS*, *HF*, *QS*, FWHM and Area represent isomer shift, hyperfine field, quadrupole splitting, full width at half maximum and area percentage of total fit, respectively.