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Charge Disproportionation in Sr0.5Bi0.5FeO3 Containing Unusually High Valence Fe3.5+

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ABSTRACT: A Sr analog of Ca0.5Bi0.5FeO3, Sr0.5Bi0.5FeO3, containing unusually high-valence Fe3.5+ ions was synthesized by using a high-pressure technique. It relieves the electronic instability due to the unusually high valence of Fe3.5+ by a single charge disproportionation (CD) transition (Fe3.5+ → 0.75Fe3+ + 0.25Fe5+) rather than the successive CD and intersite charge transfer (CT) transitions seen in Ca0.5Bi0.5FeO3. Conduction-band narrowing due to the significant bend in the Fe-O-Fe bond in the rhombohedral R-3c crystal structure stabilized the charge-disproportionated state at low temperatures. Most importantly, Bi3+ ions in Sr0.5Bi0.5FeO3 do not act as counter cations accepting oxygen holes as they do in Ca0.5Bi0.5FeO3, resulting in the absence of the intersite CT transition. The large cavity of the A-site Sr ions prevents the charge transferred Bi5+ from being stabilized. In the charge-disproportionated state the nearest-neighbor Fe3+ spins align antiferromagnetically and one quarter of the Fe3+ spins are randomly replaced by Fe5+ spins coupled ferromagnetically with the neighboring Fe3+ spins.
I. INTRODUCTION

Transition-metal ions with unusually high valence states can be stabilized in some oxides synthesized under strong oxidizing conditions.\textsuperscript{1-5} Electronic instability due to such unusually high valence states is often relieved via charge transitions and these transitions are typically accompanied by drastic changes in structural, transport, and magnetic properties. Material systems containing unusually high valence ions thus provide excellent platforms for investigating complex charge-lattice-spin couplings.

Although the typical valence states of Fe ions in oxides are 2+ and 3+, unusually high valence states of Fe ions like Fe\textsuperscript{4+} can be stabilized in some oxides and are of particular interest. Fe\textsuperscript{4+} in the perovskite CaFeO\textsubscript{3}, for instance, relieves its electronic instability by a very unusual charge change at 290 K: charge disproportionation (CD) to Fe\textsuperscript{3+} and Fe\textsuperscript{5+} (2Fe\textsuperscript{4+} → Fe\textsuperscript{3+} + Fe\textsuperscript{5+}).\textsuperscript{6} Because the strong hybridization of low-lying Fe-3d orbitals in Fe\textsuperscript{4+} with O-2p orbitals produces oxygen p holes (ligand holes, $L$) in the electronic structure, the CD is expressed as localization of the ligand holes described as $2d^5L \rightarrow d^5 + d^5L^2$. The localization of the ligand holes at the Fe sites alternately makes a rock-salt type order of the Fe\textsuperscript{3+}O\textsubscript{6} and Fe\textsuperscript{5+}O\textsubscript{6} octahedra. Fe\textsuperscript{4+} in the cubic perovskite SrFeO\textsubscript{3}, on the other hand, behaves differently. The itinerant ligand holes in SrFeO\textsubscript{3} are stabilized in the broad conduction bands due to the linear Fe-O-Fe bonds and are tolerant to delocalization.\textsuperscript{9} As the result, SrFeO\textsubscript{3} stays metallic down to low temperatures and does not undergo a charge transition.

The perovskite Ca\textsubscript{0.5}Bi\textsubscript{0.5}FeO\textsubscript{3} can be obtained by substituting Bi\textsuperscript{3+} ions for half of the Ca\textsuperscript{2+} ions in CaFeO\textsubscript{3}, and the doped electrons change the unusually high-valence Fe\textsuperscript{4+} to Fe\textsuperscript{3.5+}.\textsuperscript{10} This electron doping induces charge behaviors different from the CD in CaFeO\textsubscript{3}, and when cooled the compound shows successive transitions due to CD (Ca\textsubscript{0.5}Bi\textsubscript{0.5}Fe\textsuperscript{3.5+}O\textsubscript{3} → Ca\textsubscript{0.5}Bi\textsubscript{0.5}Fe\textsuperscript{3+}0.67Fe\textsuperscript{4.5+}0.33O\textsubscript{3}) at 250 K and inter site charge transfer (CT) between B-site Fe and A-site Bi (0.25Bi\textsuperscript{3+} + 0.33Fe\textsuperscript{4.5+} → 0.25Bi\textsuperscript{3+} + 0.33Fe\textsuperscript{3+}) at 200 K. The Bi ions in Ca\textsubscript{0.5}Bi\textsubscript{0.5}FeO\textsubscript{3} are the counter cations accepting the charge transferred from the unusually high-valence Fe ions, as in the inter site CT in BiNiO\textsubscript{3} under pressure (Bi\textsuperscript{3+}Ni\textsuperscript{3+}O\textsubscript{3} → Bi\textsuperscript{3+}0.5Bi\textsuperscript{5+}0.5Ni\textsuperscript{2+}O\textsubscript{3}).\textsuperscript{9} The CT transition occurring after the CD transition completely relieves the electronic instability of Fe\textsuperscript{3.5+} in Ca\textsubscript{0.5}Bi\textsubscript{0.5}FeO\textsubscript{3}. Both are accompanied by the changes in structural and magnetic properties, indication strong couplings of the charge, lattice and spin in Ca\textsubscript{0.5}Bi\textsubscript{0.5}FeO\textsubscript{3}.

Our primary concern is what kind of charge transitions would be induced in Bi-doped SrFeO\textsubscript{3}. Although Fe\textsuperscript{4+} in SrFeO\textsubscript{3} shows neither CD nor CT transitions, it is of interest how the instability of unusually high-valence Fe\textsuperscript{3.5+} is relieved in the presence of Bi\textsuperscript{3+} that can be oxidized to Bi\textsuperscript{5+}. In this study we prepared the novel perovskite Sr\textsubscript{0.5}Bi\textsubscript{0.5}FeO\textsubscript{3} under a high-pressure and high-temperature condition and found that at low temperatures it shows a single CD transition of the Fe\textsuperscript{3.5+} to Fe\textsuperscript{3+} and Fe\textsuperscript{5+} in a 3:1 ratio. The Bi ions in Sr\textsubscript{0.5}Bi\textsubscript{0.5}FeO\textsubscript{3}, unlike those in Ca\textsubscript{0.5}Bi\textsubscript{0.5}FeO\textsubscript{3}, did not induce an inter site CT transition. We investigated the compound’s crystal and magnetic structures, and here
we discuss the observed CD transition.

II. EXPERIMENTAL

Sr$_{0.5}$Bi$_{0.5}$FeO$_3$ was prepared by a solid-state reaction under a high-pressure and high-temperature condition. Starting materials (SrCO$_3$, Bi$_2$O$_3$, and Fe$_2$O$_3$) were well mixed and calcined at 850°C. The resultant polycrystalline sample and oxidizing agent KClO$_4$ were well ground, sealed in a platinum capsule, treated at 6 GPa and 1200 °C for 30 minutes, and then quenched to room temperature before the pressure was released.

The crystal and magnetic structures of Sr$_{0.5}$Bi$_{0.5}$FeO$_3$ were analyzed by evaluating synchrotron X-ray powder diffraction (SXRD) and neutron powder diffraction (NPD) data. The SXRD data from room temperature to 80 K were collected with a wavelength of 0.82656 Å at the beamline TPS09A at the National Synchrotron Radiation Research Center. The sample was packed into a glass capillary with an inner diameter of 0.1 mm. The obtained data was analyzed by the Rietveld method using the RIETAN-FP program. NPD measurements were performed on a sample contained in a vanadium can using the WISH diffractometer at the ISIS neutron source, Rutherford Appleton Laboratory, UK. The diffraction data were analyzed with the GSAS suite programs.

To investigate the valence and magnetic states of Fe ions in Sr$_{0.5}$Bi$_{0.5}$FeO$_3$, $^{57}$Fe Mössbauer spectroscopy measurements were carried out in a transmission geometry with a constant-acceleration spectrometer by using a $^{57}$Co/Rh radiation source. $^{57}$Fe was used to calibrate the velocity scale, the isomer shift (IS) and the hyperfine field (HF). The obtained spectra were fitted to Lorentzian functions by using the standard least-squares method.

Magnetic properties of the sample were measured with a SQUID magnetometer (MPMS Quantum Design). Resistivity was measured with a standard four-probe method by using a commercial Physical Property Measurement system (Quantum Design).

III. RESULTS AND DISCUSSION

The obtained sample was a nearly single phase (unreacted Fe$_2$O$_3 <1\%$). Room temperature SXRD peaks could be indexed with a rhombohedral $R-3c$ unit cell in the space group (No. 167). Crystal structure was analyzed by the Rietveld method with SXRD and NPD data, and the results are shown in Figures 1a and 1b. The structure parameters obtained from the analysis are listed in Table I. The rhombohedral crystal structure is slightly distorted from the cubic perovskite. The refined occupancies for the A-site Sr/Bi were respectively 0.486/0.514(3), indicating random distribution of the ions at the site. The oxygen site occupancy refined with the NPD data was 0.991(2), indicating the oxygen stoichiometry of the compound. The occupancy for oxygen was fixed to 1 in the final refinement.

Given the composition of Sr$_{0.5}$Bi$_{0.5}$FeO$_3$ with typical-valence Sr$^{2+}$, Bi$^{3+}$, and O$^{2-}$ ions, unusually high-valence Fe$^{3.5+}$ is suggested in this compound. The bond valence sum (BVS)$^{13,14}$ value calculated from the Fe-O bond lengths obtained from the structure refinement results is 3.4+, in
consistency with the nominal valence state of Fe. The unusually high valence state of Fe was also confirmed by Mössbauer spectroscopy, as shown in Figure 2. The spectrum at room temperature consists of a singlet with an IS of 0.20 mm/s, which is between the typical values for Fe$^{3+}$ ($\approx 0.54$ mm/s)$^{15}$ and Fe$^{5+}$ ($\approx 0.07$ mm/s)$^{9}$ for octahedral oxygen coordination and is also very close to the value for Fe$^{3.5+}$ observed in Ca$_{0.5}$Bi$_{0.5}$FeO$_{3}$.

The present Sr$_{0.5}$Bi$_{0.5}$FeO$_{3}$ containing unusually high-valence Fe$^{3.5+}$ is thus a Sr analog of the previously reported Ca$_{0.5}$Bi$_{0.5}$FeO$_{3}$. The compound can also be considered to be Bi$^{3+}$-doped SrFeO$_{3}$, where the doped electrons due to the substitution of Bi$^{3+}$ for Sr$^{2+}$ produces Fe$^{3.5+}$ at the B-site. The substitution also causes rhombohedral structural distortion with a significant bend (165.5(2)$^\circ$) in the Fe-O-Fe bond from the 180$^\circ$ bonding in cubic SrFeO$_{3}$. Note that the Fe-O-Fe bond angle is larger than that in orthorhombic Ca$_{0.5}$Bi$_{0.5}$FeO$_{3}$ (155.3$^\circ$).

On cooling the sample, no apparent structural phase transitions were observed. Temperature dependences of the lattice parameters and the cell volume, plotted in Figure 3, show monotonic decrease down to about 80 K. The observed behavior is in sharp contrast to that due to the successive structural phase transitions caused by the CD at 250 K and CT at 200 K in Ca$_{0.5}$Bi$_{0.5}$FeO$_{3}$.

Although no structural transition was observed, an unusual charge change occurred in the present Sr$_{0.5}$Bi$_{0.5}$FeO$_{3}$. The Mössbauer spectrum taken at 4 K (Figure 2) clearly shows a charge-disproportionated state of Fe. The spectrum consists of two sextets, with ISs of 0.43 and 0.00 mm/s, in a 3:1 ratio. These sextets are very similar to those observed in the charge-disproportionated state of CaFeO$_{3}$ and are assigned to Fe$^{3+}$ and Fe$^{5+}$. The Mössbauer results therefore reveal that the CD transition Fe$^{3.5+}$ $\rightarrow$ 0.75Fe$^{3+}$ + 0.25Fe$^{5+}$ takes place at a low temperature in Sr$_{0.5}$Bi$_{0.5}$FeO$_{3}$. Although the charge-disproportionated state in Sr$_{0.5}$Bi$_{0.5}$FeO$_{3}$ is evident, the transition temperature is difficult to determine. When we examine the temperature dependence of electrical resistivity (Figure 4) in detail, however, we see that below 230 K it deviates from the normal semiconductor behavior. In the temperature dependence of magnetic susceptibility (Figure 5b) an anomaly at about 230 K is seen. The Mössbauer spectrum taken at 200 K looks a single peak, but is much broader than the room temperature one and actually can be fitted with 3:1 components of paramagnetic Fe$^{3+}$ and Fe$^{5+}$ (Figure S2 and Table SII). Because no other anomalies were observed in temperature-dependent experimental data, the CD transition temperature of Sr$_{0.5}$Bi$_{0.5}$FeO$_{3}$ appears to be around 230 K. The absence of significant changes in the unit cell volume at the CD transition temperature is similar to the transition behaviors observed in CaFeO$_{3}$ and La$_{1/3}$Sr$_{2/3}$FeO$_{3}$.$^{16}$

It is interesting to note that the Bi$^{3+}$ substitution does not induce a CT transition in SrFeO$_{3}$, which stays metallic down to low temperatures without any charge transition, whereas it induces a CT transition in CaFeO$_{3}$, which originally shows a CD transition. Unlike the Bi ions in Ca$_{0.5}$Bi$_{0.5}$FeO$_{3}$, the Bi ions in Sr$_{0.5}$Bi$_{0.5}$FeO$_{3}$ cannot be counter cations accepting the oxygen holes from the unusually high-valence Fe ions, resulting in the absence of a CT transition. The Bi$^{3+}$ substitution causes the conduction-band narrowing, at low temperature, due to the significant bend (165.5 (2)$^\circ$) in the Fe-O-Fe bond from the 180$^\circ$ bonding in SrFeO$_{3}$. Therefore the ligand holes of Fe$^{3.5+}$ are localized at some of the Fe sites making the $d^6L^2$ electronic state but not at the Bi sites. A negative chemical pressure applied to the Bi$^{3+}$ ions (ionic radius $= 1.03$ Å for 6 oxygen coordination$^{17}$) by the large cavity of the A-site Sr$^{2+}$ ions (1.18 Å) prevents the much smaller Bi$^{5+}$ ions (0.76 Å) from being stabilized,
suppressing the intersite CT transition. In this sense, the situation is rather similar to the CD transition in La_{0.5}Sr_{0.5}FeO_{3.18} Although the Mössbauer spectrum of Sr_{0.5}La_{0.5}FeO_{3} at low temperature was analyzed with three components, their IS values suggest the essential 3:1 CD of Fe^{3+} and Fe^{5+}. The Fe-O-Fe bond angle in Sr_{0.5}Bi_{0.5}FeO_{3} (165.5(2)°) is also to that in Sr_{0.5}La_{0.5}FeO_{3} (167.8(2)°). (The crystallographic data of our Sr_{0.5}La_{0.5}FeO_{3} sample is listed in the Supporting information Table S1.) Like La_{3+} in Sr_{0.5}La_{0.5}FeO_{3}, Bi^{3+} in Sr_{0.5}Bi_{0.5}FeO_{3} does not trigger a CT transition relieving the electronic instability of Fe^{3.5+}.

In the charge-disproportionated state at low ow temperature there is no indication of ordering of the 3:1 Fe^{3+} and Fe^{5+} ions in either the SXRD or NPD patterns. In the low-temperature (5 K) NPD pattern, however, magnetic superstructure reflections are evidently included. The magnetic order of the Fe spins in the CD state is consistent with the Mössbauer spectroscopy measurement result at 4 K, where both Fe^{3+} and Fe^{5+} components consist of sextets with large HFs. Assuming that the magnetic moments of all Fe ions are the same due to the random distribution of the Fe^{3+} and Fe^{5+} ions, the observed magnetic reflections are reproduced well with a G-type antiferromagnetic structure of the B-site Fe spins and the magnetic analysis gives the refined magnetic moment of 2.01(1) μB. The refined profile of low-temperature NPD is plotted in Figure 1c and the refined structure parameters are listed in Table S2.

The proposed magnetic structure is shown in Figure 6. In the G-type antiferromagnetic structure, where the nearest-neighbor spins align in an antiparallel way, one quarter of the Fe^{3+} spin sites are randomly replaced by Fe^{5+} spins. According to the Kanamori-Goodenough rules, those Fe^{5+} spins couple ferromagnetically with the neighboring Fe^{3+} spins, and that is why the refined G-type antiferromagnetic moment is significantly reduced. Although this spin arrangement gives 8 μB per 4 Fe spins, those hypothetical ferromagnetic moments cancel out and no net magnetization would be produced due to the random distribution of the Fe^{5+} spins. This magnetic structure model is also consistent with the linear behavior observed in the isothermal M-H measurements below the CD transition temperatures (Figure 5c). The small refined magnetic moments at Fe spin sites may indicate another magnetic structure model with Fe^{5+} spin moments oriented random directions, as they have been proposed to be oriented in CeCu_{3}Fe_{4}O_{12}, which also contains Fe^{5+} at B-site in the A-site-ordered perovskite structure and shows a similar 3:1 CD of Fe^{3+} and Fe^{5+}.19 However, the present magnetic property measurement results do not support that model because neither net magnetization in the M-H measurements nor peak broadening of the Fe^{5+} Mössbauer spectrum below the CD transition temperature was observed.

The magnetic transition temperature due to charge-disproportionated Fe^{3+} and Fe^{5+} spins was difficult to determine from the magnetic susceptibility measurement (Figure 4a). Nonetheless, the observed susceptibility blow about 150 K shows large hysteresis between the field-cooled (FC) and zero-field-cooled (ZFC) mode measurements. The Mössbauer spectrum taken at 150 K apparently contains magnetically ordered sextet components (Figure S2). Therefore the antiferromagnetic transition temperature of Sr_{0.5}Bi_{0.5}FeO_{3} appears to be about 150 K, which is lower than the CD transition temperature. The behavior that the magnetic ordering of Fe^{3+} and Fe^{5+} spins occurs and is followed by the CD transition is similar to the behaviors observed in CaFeO_{3} and Ca_{2}FeMnO_{6} [20] and is different from the simultaneous charge and spin transitions in CaCu_{3}Fe_{4}O_{12}.21
The behavior is also very different from the successive charge transitions in Ca$_{0.5}$Bi$_{0.5}$FeO$_3$ with an idle spin state between the CD and intersite CT transition temperature.\textsuperscript{22}

**IV. SUMMARY**

The novel compound Sr$_{0.5}$Bi$_{0.5}$FeO$_3$, containing unusually high-valence Fe$^{3.5+}$ ions, was synthesized under a high-pressure and high-temperature condition. Rietveld refinements of SXRD and NPD data confirmed that the compound crystallized in a distorted perovskite structure with the rhombohedral space group $R\bar{3}c$. Mössbauer spectroscopy study revealed that CD ($\text{Fe}^{3.5+} \rightarrow 0.75\text{Fe}^{3+} + 0.25\text{Fe}^{5+}$) took place below 230 K. The charge-disproportionated Fe$^{3+}$ and Fe$^{5+}$ spins magnetically order at about 150 K, which is below the CD transition temperature. The magnetic structure was solved by a combined analysis of low-temperature NPD profile and isothermal magnetization data. The nearest-neighbor Fe$^{3+}$ spins align antiferromagnetically, giving the G-type antiferromagnetic structure and one quarter of the Fe$^{3+}$ spin sites are randomly replaced by Fe$^{5+}$ spins coupled ferromagnetically with the neighboring Fe$^{5+}$ spins. The random distribution of the Fe$^{5+}$ spins is consistent with the linear behavior evident in the $M-H$ measurements.

Unlike Ca$_{0.5}$Bi$_{0.5}$FeO$_3$, which shows successive CD and intersite CT transitions, the Sr analog Sr$_{0.5}$Bi$_{0.5}$FeO$_3$ shows a single CD transition ($\text{Fe}^{3.5+} \rightarrow 0.75\text{Fe}^{3+} + 0.25\text{Fe}^{5+}$) relieving the electronic instability due to the unusually high valence of Fe$^{3.5+}$. A significant bend in the Fe-O-Fe bond in the rhombohedral $R\bar{3}c$ crystal structure makes the conduction bands narrow, stabilizing the charge-disproportionated state at low temperatures. The Bi$^{3+}$ ions in Sr$_{0.5}$Bi$_{0.5}$FeO$_3$ cannot be counter cations accepting oxygen holes as they do in Ca$_{0.5}$Bi$_{0.5}$FeO$_3$, resulting in the absence of an intersite CT transition. A negative chemical pressure applied to the Bi$^{3+}$ ions by the large cavity of the A-site Sr$^{2+}$ ions prevents the much smaller Bi$^{5+}$ ions from being stabilized, suppressing the intersite CT transition.

**References**

Because no reliable ionic radius for Bi$^{3+}$ for 12 oxygen coordination was reported, we tentatively use the ionic radii for 6 oxygen coordination.
Figures

Figure 1. Rietveld refinement profiles for Sr_{0.5}Bi_{0.5}FeO_{3}. (a) Room-temperature SXRD data. The top and bottom vertical bars respectively indicate the diffraction peak positions for Sr_{0.5}Bi_{0.5}FeO_{3} and impurity Fe_{2}O_{3}. (b) Room-temperature ND data. The top bars indicate the nuclear diffraction of Sr_{0.5}Bi_{0.5}FeO_{3}. The middle and bottom bars respectively show the nuclear and magnetic reflection of impurity Fe_{2}O_{3}. (c) ND data collected at 4 K. The top and second vertical bars respectively show the nuclear and magnetic reflections of Sr_{0.5}Bi_{0.5}FeO_{3}. The third and bottom vertical bars respectively show the nuclear and magnetic reflections of impurity Fe_{2}O_{3}. 
Figure 2. Mössbauer spectrum of Sr$_{0.5}$Bi$_{0.5}$FeO$_3$ at room temperature (top panel) and 4 K (bottom panel). The black circles show experimental data and the solid lines show the fittings.

Figure 3. Temperature dependence of the lattice parameters $a$ and $c$ which is which? and cell volume $V$ of Sr$_{0.5}$Bi$_{0.5}$FeO$_3$ in hexagonal rhombohedral $R$–3c lattice. Comment – we might get useful information from lattice strains. Try plotting $a$ and $c/\sqrt{6}$ on the same scale, and also plot the strain $(a - c/\sqrt{6})/a$ to see if this shows the transitions.
Figure 4. Temperature dependence of the electrical resistivity as a plot of $\log \rho$ versus $1000/T$. The blue dashed line represents a typical semiconductor change given by an Arrhenius equation.
Figure 5. (a) Temperature dependence of the magnetic susceptibility of Sr$_{0.5}$Bi$_{0.5}$FeO$_3$ in a 10 kOe external magnetic field. The red and blue curves respectively represent ZFC and FC susceptibility. (b) Differential plots of the magnetic susceptibility data. (c) Isothermal magnetization curves measured at temperatures between 300 K and 5 K.

Comment – we should plot the average G type magnetic structure somewhere also

Figure 6. Schematic drawing of the proposed magnetic structure of Sr$_{0.5}$Bi$_{0.5}$FeO$_3$. The green and blue arrows respectively represent spins of charge-disproportionated Fe$^{3+}$ and Fe$^{5+}$.

**TABLES**

**Table I.** Refined structural parameters of Sr$_{0.5}$Bi$_{0.5}$FeO$_3$ at room temperature.

In the structure refinement the rhombohedral crystal structure was analyzed with the hexagonal cell. The BVS results calculated from the cation-O bond lengths are also listed. *u*iso units

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<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{iso}$</th>
<th>Occupancy</th>
<th>BVS</th>
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Space group: $R$–3c. $a = 5.5243$ (2) Å, $c = 13.5306$ (7) Å, and $R_{wp} = 2.7\%$.

**Table II.** Mössbauer parameters for Sr$_{0.5}$Bi$_{0.5}$FeO$_3$ at room temperature and 4 K.

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<td>------------------</td>
<td>------------</td>
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<tr>
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<td></td>
<td>Fe$^{5+}$</td>
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**Supplemental Information**

Figure S1. Refinement profiles for Sr_{0.5}La_{0.5}FeO_3 against room temperature XRD data. The purple vertical bars indicate the diffraction peak positions for Sr_{0.5}La_{0.5}FeO_3.

Figure S2. Mössbauer spectrum measured at different temperatures. The black cycles indicate the counts and the solid lines respectively represent fit sum (red), green (Fe^{3+}) and blue (Fe^{5+}).
**Table S1.** Refined structure parameters for Sr$_{0.5}$La$_{0.5}$FeO$_3$ against room temperature SXRD data. In the structure refinement the rhombohedral crystal structure was analyzed with the hexagonal cell. The cation (M)-O bond lengths calculated for the refinement result and the BVS are also listed.

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<tr>
<th>Atom</th>
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<th>$x$</th>
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<th>$z$</th>
<th>$U_{iso}$</th>
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Space group: $R$–3$c$. $a = 5.50701$ (8) Å, $c = 13.4086$ (3) Å, and $R_{wp} = 2.4\%$.

**Table SII.** Mössbauer parameters for Sr$_{0.5}$Bi$_{0.5}$FeO$_3$ at 200 K.

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<tbody>
<tr>
<td>Fe$^{3+}$</td>
<td>0.31</td>
<td>0.57</td>
<td>74.2</td>
</tr>
<tr>
<td>Fe$^{5+}$</td>
<td>-0.05</td>
<td>0.38</td>
<td>25.8</td>
</tr>
</tbody>
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