# Charge Disproportionation in Perovskite Iron Oxides

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## Abstract

The physical properties of perovskite iron oxides are closely related to the network of $FeO_6$ octahedra. The charge disproportionation ($2Fe^{4+} \rightarrow Fe^{3+} + Fe^{5+}$), not observed in $SrFeO_3$, occurs in the oxides being cut the network of $Fe^{4+}O_6$ octahedra, for example, by intrduction of $Fe^{3+}$ by substitution La for Sr and change in the dimension by insertion of SrO layer. When Co is substituted 40% of Fe in $Sr_3Fe_2O_7$, the magnetic order changes to ferromagnetic from antiferromagnetic and charge disproportionation is suppressed.

*Key words:* charge disproportionation; perovskite iron oxides; Mössbauer measurement

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## 1. Introduction

Perovskite and related iron oxides with the high-spin $d^4$ display a wide variety in their magnetic and electronic properties. The physical properties of perovskite iron oxides are related to the network of $FeO_6$. It is known that the properties of these type of oxides are affected by the number of layers of $FeO_6$ octahedra. The general chemical formula can be written as $A_{n+1}Fe_nO_{3n+1}$, where $n$ is the number of layers of $FeO_6$ octahedra in perovskite iron oxides; this is the so-called Ruddlesden-Popper phase [1]. The charge disproportionation (CD, $2Fe^{4+} \rightarrow Fe^{3+} + Fe^{5+}$) has not been observed in $SrFeO_3$ with $n = \infty$[2], however CD occurs in $Sr_3Fe_2O_7$ with $n = 2$ [3]. Substitution of another element at the $A$ site or at the Fe site induces the changes in magnetic properties and CD; for example, $La_{1/3}Sr_{2/3}FeO_3$ show CD [4] and $SrFe_{1-x}Co_xO_3$ ($x \geq 0.2$) shows a change to ferromagnet [5].

## 2. Results and discussion

For the $^{57}$Fe Mössbauer spectroscopy, $^{57}$Co in Rh was used for a $\gamma$-ray source and velocity scale is relative to $\alpha$-Fe at room temperature. The $^{57}$Fe Mössbauer spectra were obtained at 4.5 K without and under the external magnetic field of 7 T applied longitudinally to the $\gamma$-ray propagation direction.

As shown in Fig. 1, the Mössbauer spectra under 7 T are different between each column. The Mössbauer spectra of $Sr_3Fe_2O_7$ and $SrFeO_3$ (no substitution) in the middle column show split of two or three subspectra under 7 T. However the spectra obtained from the La substituted oxides as shown in the left column don't show such split under 7 T. On the other hand, as shown in the right column the spectrum of $Sr_3Fe_{1.2}Co_{0.8}O_7$ without the external magnetic field shows no CD, and the spectrum under 7 T shows the reduction of the hyperfine field and the 2nd and 5th absorption peaks are almost supressed.

The direction of iron magnetic moment is just opposite to the direction of the hyperfine field and the intensity of the 2nd and 5th absorption peaks generally depends on the angle between the directions of the hyperfine field and $\gamma$-ray. When the hyperfine field is parallel or perpendicular to $\gamma$-ray, the intensity ratio of 6 absorption peaks is 3:0:1:1:0:3, or 3:4:1:1:4:3, respectively. The Mössbauer spectrum of $Sr_3Fe_{1.2}Co_{0.8}O_7$ under 7 T shows the reduction of the intensities of the 2nd and 5th absorption peaks, So all moments of Fe in $Sr_3Fe_{1.2}Co_{0.8}O_7$ align ferromagnetically to the $\gamma$-ray direction. The Mösbauer spectra of $Sr_3Fe_2O_7$

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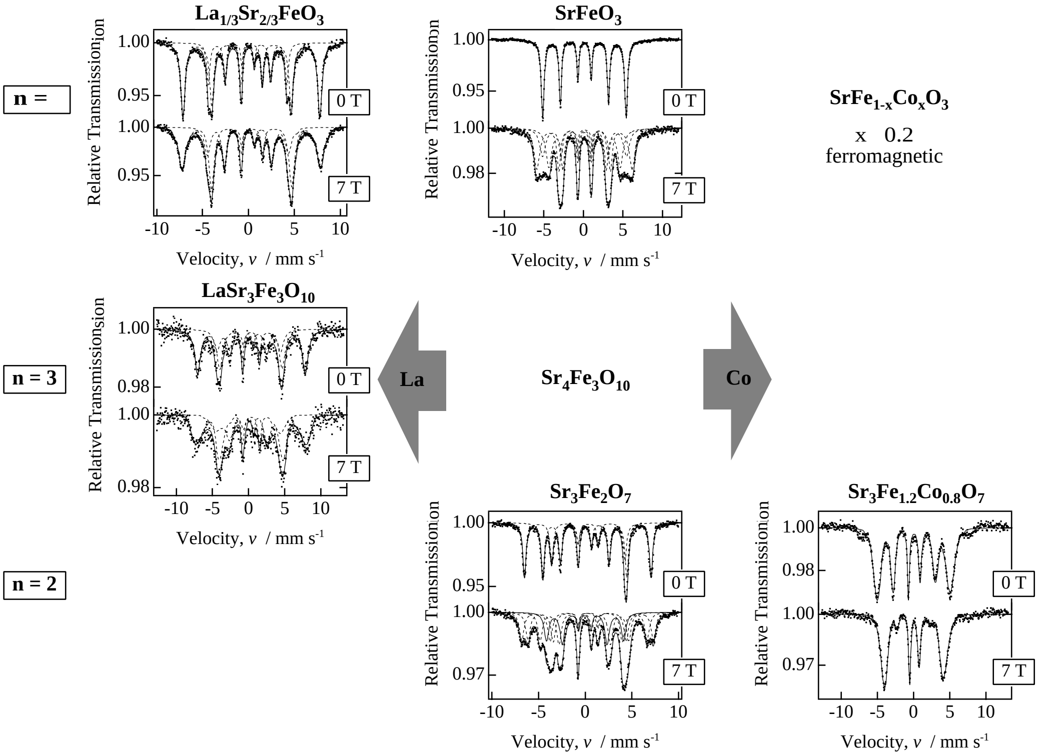

Fig. 1. The $^{57}$Fe Mössbauer spectra of perovskite iron oxides without and with the external magnetic field of 7 T at 4.5 K. The arrangement of spectra is relative to the structural dimension and substitutions of La and Co into *A*and Fe site.

at 4.5 K under 7 T show the four subspectra. Each component of $Fe^{3+}$ and $Fe^{5+}$ splits into two absorption lines, the difference between magnitudes of the observed hyperfine fields is smaller than twice of the external magnetic field. From the result, we can conclude that the antiferromagnetic interactions between the same spins ($Fe^{3+}$ and $Fe^{3+}$, $Fe^{5+}$ and $Fe^{5+}$) are very strong. The similar features were found in the Mössbauer studies of $CaFeO_3$ [6] and $SrFeO_3$ (Fig. 1) which have helical magnetic structure along $\langle 111 \rangle$ direction. At this point we advocate that the spin structure of $Sr_3Fe_2O_7$ may also be helical. The spectral features of $La_{1/3}Sr_{2/3}FeO_3$ and $LaSr_3Fe_3O_{10}$ at 4.5 K under 7 T are quite different from that of $Sr_3Fe_2O_7$. From the relative intensity of 2nd and 5th absorption peaks against 1st and 6th peaks, the moments of Fe in $La_{1/3}Sr_{2/3}FeO_3$ and $LaSr_3Fe_3O_{10}$ cant almost perpendicularly against the external magnetic field. The spin structure of $La_{1/3}Sr_{2/3}FeO_3$ is clarified as collinear from the transmission electron microscopic study [7]. The Mössbauer spectra of $LaSr_3Fe_3O_{10}$ suggest the existence of the same interactions with the case of $La_{1/3}Sr_{2/3}FeO_3$. Therefore we can conclude that $LaSr_3Fe_3O_{10}$ has a collinear spin structure as the case of $La_{1/3}Sr_{2/3}FeO_3$.

## 3. Conclusion

CD, which has not been observed in $SrFeO_3$ with cubic perovskite structure ($n = \infty$), occurs in the oxides being cut the network of $FeO_6$ octahedra, for example, by intrduction of $Fe^{3+}$ by substitution La for Sr and change in the dimension by insertion of SrO layer. However there is difference in the spin structure between the oxides changed structure and that substututed La for Sr. On the other hand, when Co is substituted 40% of Fe in $Sr_3Fe_2O_7$, the magnetic order changes to ferromagnetic from antiferromagnetic and CD is suppressed.

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