Cédric Tassel (Doctor Course student : 3rd year)(Supervised by Professor Hiroshi Kageyama)
Department of Chemistry
Graduate School of Science,
Kyoto University, Kyoto 606-8502, Japan.

Research Summary:

Hydride reduction mechanism for $Sr_{0.2}Ba_{0.8}FeO_2$: a derivative of infinite layer structures

Purpose and Background

We recently developed the synthesis of an infinite layer structure $SrFeO_2$ with iron in a square planar coordination from $SrFeO_3$, using CaH_2 as a powerful reductant [1]. This not only extended the oxygen vacancy of $SrFeO_{3-x}$ ($0 \leq x \leq 0.5$) to $x = 1$ but also provided an important impact to multidisciplinary research fields [2, 3, 4]. Significance of this work includes (1) unprecedented square planar coordination in iron oxide, (2) low temperature (~130-400°C) oxygen extraction/insertion and (3) structural relevance to high-Tc superconducting cuprates ($SrFeO_2$ is isostructural with $SrCuO_2$). Using the same synthetic strategy, a spin ladder structure $Sr_3Fe_2O_5$ (Fig. 1b) again with a square planar coordination geometry was obtained from $Sr_3Fe_2O_7$ [5, 6].

Among the interesting features in these iron oxides, (2) is of special importance for developing new oxygen ion conductors which may find potential industrial applications such as solid oxide fuel cells (SOFCs). Utmost challenge in this field is lowering temperatures of oxygen migration in solids. In this regard, extremely low temperature transformation between $SrFeO_3$ and $SrFeO_2$, and between $Sr_3Fe_2O_7$ and $Sr_3Fe_2O_5$ will provide a fundamentally new mechanism and new concept of oxygen ion conductivity. In order to investigate how such a transformation occurs at low temperatures, we performed 'in-situ' X-ray diffraction experiments at BL02B2 based on the proposal 2008A1713 for $SrFeO_2$ and 2008B1736 for $Sr_3Fe_2O_5$. It was found that the $SrFeO_3$ phase with octahedral first converts to the $SrFeO_{2.5}$ phase with octahedra/tetrahedra, and then to $SrFeO_2$ with square planes. No intermediate phase was detected between

SrFeO$_{2.5}$ and SrFeO$_2$. In the same way, the Sr$_3$Fe$_2$O$_7$ phase with octahedra first converts to the Sr$_3$Fe$_2$O$_6$ phase with pyramids and then to Sr$_3$Fe$_2$O$_5$ with square planes, and no intermediate phase was detected between Sr$_3$Fe$_2$O$_6$ and Sr$_3$Fe$_2$O$_5$. These observations clearly indicate a drastic rearrangement of oxygen frameworks is possible at low temperatures [7].

The motivation of this proposal was to investigate the reaction process in brand new iron oxides CaFeO$_2$ [8] and BaFeO$_2$ [9]. The former was prepared from the reaction of a brownmillerite phase CaFeO$_{2.5}$ with CaH$_2$, while the latter by the reaction of a perovskite phase BaFeO$_3$ with NaH. The structural refinement of the synchrotron (BL02B2) and neutron diffraction data revealed [8] that CaFeO$_2$ preserves the infinite-layer like character of SrFeO$_2$; however the FeO$_4$ polyhedrons distort heavily to tetrahedrons and rotate along the c-axis, resulting in the $\sqrt{2}a*\sqrt{2}a*c$ superstructure (Fig. 3a). The heavily distorted FeO$_4$ square planar geometry is very unusual for compounds with d^6 electron configurations [8]. On the contrary, the structure of BaFeO$_2$ contains three types of iron sites with different coordination geometries, FeO$_6$ octahedron, FeO$_4$ or FeO$_3$ plane (i.e., rhombus and triangular coordination), and FeO$_6$ octahedron with substantially oxygen deficiency. These polyhedra are arranged in an ordered manner, resulting in the 2$a*$2$a*c$ superstructure (Fig. 1).

Now that CaFeO$_2$ and BaFeO$_2$ have derivative structures from a perfect FeO$_4$ square planar geometry and different way of interconnections among polyhedra, it would be very interesting to investigate how such changes in local coordination affect the reaction mechanism or oxygen diffusion process during low-temperature reduction. The in situ study of hydride reduction with oxides provides an unique opportunity to answer these questions. Possibly, we may observe a metastable intermediate phase which is not detectable by 'ex-situ' XRD experiments. We will study the reduction process against temperatures. Comparison of the reaction process and speed between an ideal FeO$_4$ square planar coordination and its derivatives will be essential for optimization and designing of high-performance oxygen ion conductors with reduced working temperatures.

For this beam time allocation, we investigated the reaction conditions and pathway of the hydride reduction of Sr$_{0.2}$Ba$_{0.8}$FeO$_{2.5}$ using CaH$_2$. The strontium substituted samples have the advantage to be synthesizable in 3 days using CaH$_2$ at 320°C and thus are comparable with SrFeO$_2$ and Sr$_3$Fe$_2$O$_5$ synthesized using similar conditions. Pure

BaFeO$_2$ is synthesizable using NaH but its reaction conditions appear to be very complex in addition of its instability. The study of the reaction from CaFeO$_{2.5}$ to CaFeO$_2$ was preliminary studied in our laboratory. The synthesis of CaFeO$_2$ is achieved within one week at 280°C however all attempts to accelerate the reaction process by increasing temperature failed.

Experimental Method

Sr$_{0.2}$Ba$_{0.8}$FeO$_2$ is usually synthesized using the brownmillerite compound Sr$_{0.2}$Ba$_{0.8}$FeO$_{2.5}$ with CaH$_2$ at 320°C for 3 days. The brownmillerite phase is synthesized from the reduction of the perovskite Sr$_{0.2}$Ba$_{0.8}$FeO$_3$ by using H$_2$ gas flow at high temperature. Powders are mixed thoroughly in an argon filled glove box and pelletized. The pellets are then inserted in Pyrex tubes and sealed under vacuum. For synchrotron experiment, a similar process was used and the mixture was inserted in a 0.1 mm of diameter sealed capillary.

As the normal reaction conditions are too long for the allocated beam time we decided to perform the reaction at 350°C and accelerate the reaction process. This overheating technique was previously used for SrFeO$_2$, which is usually synthesized in one day at 280°C and was studied at 375°C.

In Spring-8, the temperature was calibrated to 350°C using a thermocouple. Then, the capillary was set up several successive patterns were collected for 5 minutes.

- Sr$_{0.2}$Ba$_{0.8}$FeO$_3$
The perovskite peaks are rapidly decreasing with time (Fig. 2) while the main peaks of the brownmillerite are rising. The CaH$_2$ peaks are also progressively disappearing. We were not able to observe the formation on any superstructure at this level and no Sr$_{0.2}$Ba$_{0.8}$FeO$_2$ peaks were observed. The loss of CaH$_2$ in the mixture led us to use a new capillary to observe the reduction from Sr$_{0.2}$Ba$_{0.8}$FeO$_{2.5}$ to Sr$_{0.2}$Ba$_{0.8}$FeO$_2$.

- Sr$_{0.2}$Ba$_{0.8}$FeO$_{2.5}$
The figure 3a is showing that the brownmillerite (mother compound) peaks are greatly decreasing within 30 minutes as well as the CaH$_2$ peaks. Within the presented theta range, the infinite layer structure peaks should have appeared. CaO peaks were observed at 18°. Absence of Sr$_{0.2}$Ba$_{0.8}$FeO$_2$ peaks and decreasing amount of brownmillerite phase

suggest that the mother compound is in fact destroying. This can be witnessed by watching the Fe metal formation at higher angles (Figure 3b) and its main peak is shown around 22°. The reaction temperature is thus too elevated.

Conclusion

Here, we showed that the temperature range for the reaction is very small compared with $SrFeO_2$. The reaction was observed for a wide range of temperature 200°C-450°C [10]. In the case of $SrFeO_2$, the sample can be synthesized within 40 minutes. This also demonstrates that the *A* site cation is playing an important role in oxygen diffusion in perovskites as well as indicates that the reaction mechanism changes in Barium substituted samples. Further investigations to understand the genuine mechanism of oxygen diffusion in these materials are needed.

[1] Tsujimoto et al., Nature 450, 1062 (2007).
[2] 朝日新聞、毎日新聞、読売新聞、産経新聞、日刊工業新聞、京都新聞、科学新聞，化学工業日報など.
[3] Chemstry and Industry, 24 Dec, 2007, Chemical & Engineering News, 14 Dec 2007, Chemistry World, 1 Jan 2008
[4] Jürgen Köhler, Angew. Chem. Int. Ed 47 (2008) 2.
[5] H. Kageyama et al., Angew. Chem. Int. Ed., 47, 5740 (2008).
[7] Tassel et al., in preparation.
[8] Tassel et al., J. Am. Chem. Soc. 130, 3764 (2008). Tassel et al., J. Am. Chem. Soc., 2009, 131 (1), 221–229.
[9] T. Yamamoto et al., in preparation.
[10] Tassel et al. Proceedings of the 10th Conference on Ferrites, 32-34 (2009).
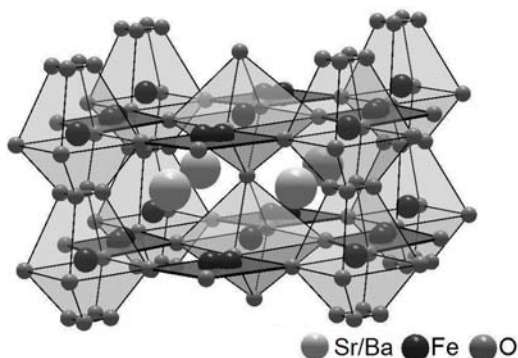
Figure 1. Structure of $Sr_{0.2}Ba_{0.8}FeO_2$

Sr/Ba ● Fe ● O

Figure 2. In-situ SXRD of $Sr_{0.2}Ba_{0.8}FeO_3$ with CaH_2 at 350˚C.
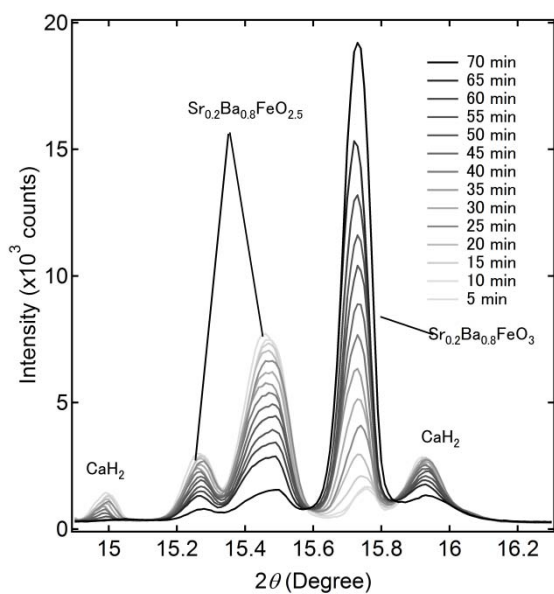
Figure 3. In-situ SXRD of $Sr_{0.2}Ba_{0.8}FeO_{2.5}$ with CaH_2 at 350˚C.