# Visualization of fast oxygen deintercalation reaction using time-resolved X-ray diffraction

Elucidating the mechanisms behind chemical reactions is a key challenge in materials chemistry as it facilitates the creation of compounds with desired structures or optimization of reactions for functional uses. However, reactions in solid-state crystalline compounds are poorly understood as compared to molecular reactions. This is partly because solid-state reactions generally require high temperatures, making the *in situ* monitoring of these reactions relatively difficult. Inhomogeneous reactions derived from the differences in surface and bulk states, as well as the existence of numerous atoms in crystals, also hinder precise analyses of reactions in solid states. Development of *in situ* measurement techniques is necessary to achieve the rational design of solid-state compounds and their reactions.

*In situ* X-ray diffraction (XRD) is a powerful tool for monitoring reactions in bulk materials, and the recent development of synchrotron X-rays has facilitated access to high-resolution data within a short time window. Time-resolved synchrotron XRD measurements have been used to investigate many reactions in crystalline phases, such as hydrothermal reactions, gas absorption, and solid-gas catalytic reactions. However, the development of a time-resolved XRD measurement of a solid–gas reaction that can precisely reveal the structural evolution on a sub-second scale remains a challenge. When the time scale of the measurement increases, intermediate phases can be captured with a shorter lifetime. This affords further prospects to optimize the reactions and/or synthesize metastable structures.

This study focused on the Ruddlesden–Popper layered perovskite $Sr_3Fe_2O_{7-\delta}$, which has recently attracted attention as a high-performance oxygen storage material. A reversible topochemical redox reaction has been observed between $Sr_3Fe_2O_{7-\delta}$ ($\delta \approx 0.4$) and $Sr_3Fe_2O_6$ ($\delta = 1.0$) under $O_2$ and $H_2$ at 773 K. The perovskite also exhibits excellent performance as an environmental catalyst material. Previously, we revealed that Pd loading dramatically promotes the oxygen release rate and decreases the release temperature under $H_2$ flow on $Sr_3Fe_2O_{7-\delta}$ ($\delta \sim 0.4$); however, the reaction pathways and structural evolution during the reduction remain unelucidated.

Therefore, we aimed to observe the actual reduction steps of $Sr_3Fe_2O_{7-\delta}$ by $H_2$ gas and the deintercalation of oxygen at SPring-8 **BL02B2** (Fig. 1). During the measurements, a capillary into which a powder sample was introduced was connected to a gas atmosphere control device. This apparatus was originally developed for the *in situ* observation of the structure of gas absorption and release of coordination polymer complexes [3]. We visualized the solid–gas reaction pathways by synchronizing the gas introduction and XRD measurements [4].

To improve the reproducibility of the reaction, the sample was subjected to multiple redox cycles at 700°C as a pretreatment. The sample in the oxidation state was then set at 500°C in vacuum, and $H_2$ gas was introduced 3 s after the start of the time-resolved XRD measurement. The XRD patterns near the main peaks obtained at intervals of 100 ms are shown in Figs. 2(a) and 2(b). The horizontal and vertical axes correspond to time and diffraction angle ($2\theta$), respectively. Measurements were performed for pristine $Sr_3Fe_2O_{6.6}$ and Pd-loaded $Sr_3Fe_2O_{6.6}$. In the case of both samples, the peaks shifted to the low-angle side immediately after the introduction of $H_2$, indicating that the reaction proceeded because of the introduction of the gas. The reaction took approximately 30 s to complete for the unsupported sample; however, for the Pd-supported sample, the reaction was remarkably accelerated and completed within a few seconds.

More importantly, the peak shifted continuously for the unloaded sample, whereas a discontinuous jump in the peak was observed for the Pd-loaded sample. This implies that a first-order phase transition of the structure occurred in the Pd-loaded sample,
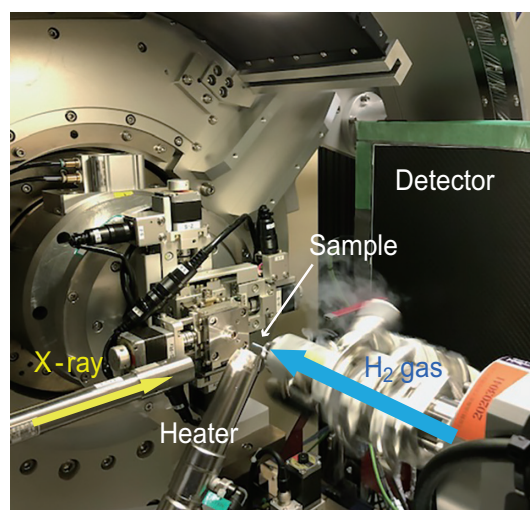


Fig. 1. Experimental setup around the sample at SPring-8 BL02B2.

whereas the structure relaxed continuously (second-order phase transition-like) in the pristine sample. This indicates that the reduction rate at the surface is slower than the diffusion of oxide ions in the bulk, and the structure is continuously relaxed at each stage of reduction in the unsupported material. Meanwhile, in the Pd-loaded sample, the reduction rate at the surface is dramatically accelerated, and the structural relaxation cannot keep pace with the reduction. Therefore, in the Pd-loaded sample, the compound was reduced to $Sr_3Fe_2O_6$ before the structural relaxation was completed, and a first-order phase transition to the stable phase was considered to have occurred. As expected, a dynamic intermediate phase, $Sr_3Fe_2O_6$ with random oxygen defects (Fig. 2(e)) appeared before the phase transition.

In this study, owing to advances in measurement techniques, we successfully captured rapid phenomena that were previously impossible to observe. Elucidation of the reaction pathway in $Sr_3Fe_2O_{7-\delta}$ is important for establishing design guidelines for future oxygen storage catalysts. Furthermore, the fact that the reaction pathway can be manipulated by surface modification is important for future exploration of materials. In other words, the reaction pathway may be selected by the surface modification of inorganic solids, just as the reaction pathway can be selected using functional groups in organic reactions. In the present reaction, we ultimately obtained the same phase despite changing the reaction pathway because of the high reaction temperatures involved. However, we anticipate that the selective synthesis of metastable phases that are inaccessible by ordinary reactions will be realizable in the future via the appropriate selection of reaction systems and temperatures.
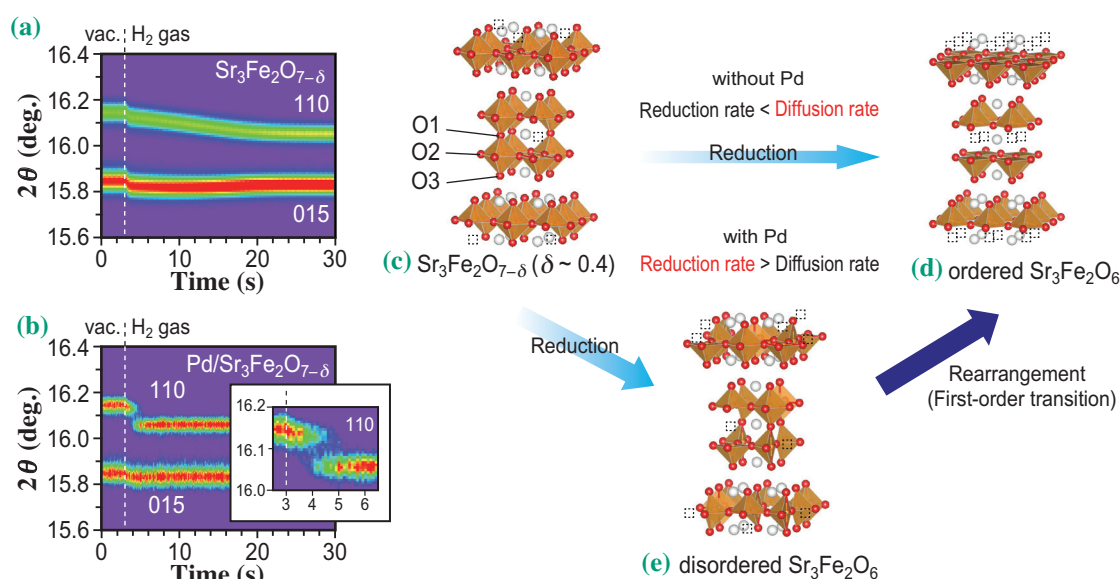


Fig. 2. Time-resolved XRD patterns for the reduction of (a) $Sr_3Fe_2O_{7-\delta}$ and (b) $Pd/Sr_3Fe_2O_{7-\delta}$ [4]. Structures of (c) $Sr_3Fe_2O_{6.6}$, (d) ordered $Sr_3Fe_2O_6$, (e) disordered $Sr_3Fe_2O_6$.

Takafumi Yamamoto

Laboratory for Materials and Structures,
Tokyo Institute of Technology

Email: yama@msl.titech.ac.jp

References
[1] Y. Tsujimoto *et al.*: Nature **450** (2007) 1062.
[2] M. A. Hayward and M. J. Rosseinsky: Nature **450** (2007) 960.
[3] S. Kawaguchi *et al.*: J. Synchrotron Rad. **27** (2020) 616.
[4] *T. Yamamoto, S. Kawaguchi, T. Kosuge, A. Sugai, N. Tsunoda, Y. Kumagai, K. Beppu, T. Ohmi, T. Nagase, K. Higashi, K. Kato, K. Nitta, T. Uruga, S. Yamazoe, F. Oba, T. Tanaka, M. Azuma and S. Hosokawa: Adv. Sci.* **10** (2023) 2301876.