



	<b>Experiment title:</b> In-situ studies of high temperature oxidation/reduction reactions; fast time resolved in-situ powder diffraction experiments.	<b>Experiment number:</b> CH1005
<b>Beamline:</b>	<b>Date of experiment:</b> from: 27 April 2001 to: 2 May 2001	<b>Date of report:</b> 4 March 2002
<b>Shifts:</b> 12	<b>Local contact(s):</b> Dr. Jon Are Beukes	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): <b>*Dr. Poul Norby and *Prof. Helmer Fjellvåg</b> Department of Chemistry, University of Oslo, Norway		

## Report:

(ESRF Highlights 2001: **Fast time resolved *in-situ* powder diffraction studies of high temperature oxidation/reduction reactions** P. Norby (a), H. Fjellvåg (a), H. Emerich (b)  
(a) Department of Chemistry, University of Oslo (Norway), (b) SNBL, ESRF)

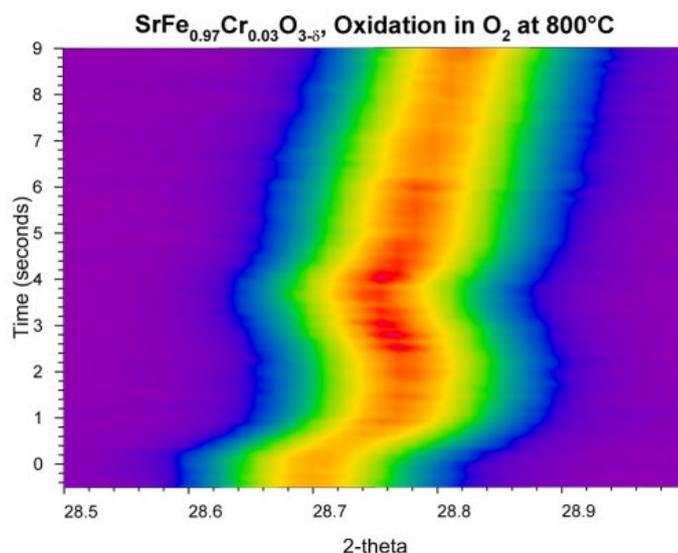
In order to perform fast time resolved *in-situ* powder diffraction experiments of synthesis and chemical reactions, a Rotating Slit system for the MAR345 imaging plate system has been developed for BM01B (SNBL). A screen with a wedge-shaped opening is rotated in front of the MAR345 image plate detector. By varying the slit size and the rotation speed, the time resolution can be adjusted. *In-situ* powder diffraction data have been collected with a time resolution around 100ms.

The Rotating Slit system allows for instance time resolved *in-situ* powder diffraction studies of fast oxidation/reduction reactions of oxygen ion conducting perovskite type materials at high temperature, 400-800°C. For high temperature applications, perovskite type oxides with composition  $(A_{1-x}A'_x)BO_{3\pm\delta}$ , (A=La,Y...; A'= Sr,Ca...; B=Mn,Fe,Co...) are of interest in connection with catalysis, oxygen permeable membranes and Solid Oxide Fuel Cells. At low temperature they are of interest e.g. with respect to colossal magneto-resistance. For these materials, properties such as catalytic activity, magnetism and oxygen ion conductivity, are closely related to oxygen stoichiometry, crystal structure and redox properties.

The oxidation/reduction reactions are of topotactic nature and these reactions are completed within a few seconds at 800°C. Therefore very fast data collection is required. At the same time, high quality powder diffraction data must be collected in order to monitor structural changes during the reaction, preferable by means of Rietveld analysis.

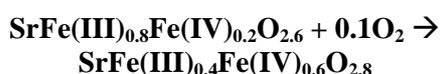
A capillary based micro reaction cell, allowing a flow of gas to pass through the sample, was used for the experiments [1,2]. Using a remotely controlled three-way valve, abrupt changes between nitrogen and oxygen gas can be achieved, allowing kinetic information to be extracted from variation of intensity or position of selected Bragg reflections. Samples were contained in 0.7-1mm quartz glass capillaries mounted in a Swagelok fitting. The sample was heated using a hot air blower.

Results are presented for oxidation of  $\text{SrFe}_{0.97}\text{Cr}_{0.03}\text{O}_{2.6}$  at 700-800°C. Switching from nitrogen to oxygen atmosphere is done while the slit is rotating continuously in front of the imaging plate (one rotation in 15 seconds). **Figure 1** shows the changes in one of the reflections as the oxidation proceeds at 800°C. The gas flow was switched from  $\text{N}_2$  to  $\text{O}_2$  at time  $t=0$ , and powder diffraction data were integrated to provide time resolution of 100 ms. An almost instantaneous change in the diffraction pattern is observed.



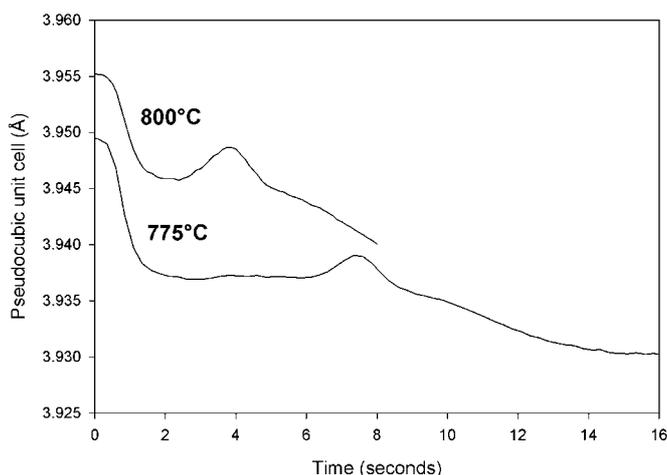
**Figure 1.** Changes in position and intensity of one diffraction peak during oxidation at 800°C

During oxidation of perovskite oxides the unit cell volume normally decreases. This is caused by shortening of the metal-oxygen bond on increased valence state of the cation, together with efficient packing of coordination polyhedra. As an example, consider the oxidation of  $\text{SrFeO}_{2.6}$ :



Typically the unit cell decrease mirrors the variation in oxygen stoichiometry. For the present oxidation process the time resolved data reveal an unexpected increase in the pseudo-cubic unit cell parameter (using LeBail profile refinement) for an intermediate time interval (**Figure 2**). The oxidation process proceeds hence in two steps. After an initial fast decrease, a plateau is reached, most visible at 775°C. A maximum in the unit cell volume is encountered before the final (slower) decrease occurs. The same general features are observed at 700°C, where the process is much slower.

So far thermogravimetric experiments have not shown mass variations indicating a two-step oxidation process. The reactions are too fast for *in-situ* neutron powder diffraction studies that otherwise could determine the time evolution of the atomic coordinates for the light oxygen atoms. It is presently proposed that the expansion anomaly is caused by redistribution of oxygen vacancies, thereby changing the relative amount of lower coordinated  $\text{MO}_4$  tetrahedra and  $\text{MO}_5$  square pyramids. Forthcoming *in-situ* synchrotron X-ray diffraction experiments will hopefully solve this intriguing problem.



**Figure 2.** Unit cell parameter (pseudo cubic) of  $\text{SrFe}_{0.97}\text{Cr}_{0.03}\text{O}_{3-\delta}$  during oxidation at 775 and 800°C.

## References

- [1] P. Norby, *J. Amer. Chem. Soc.*, **119**, 5215-5221 (1997).
- [2] E. Krogh Andersen, I.G. Krogh Andersen, P. Norby and J.C. Hanson *J. Solid St. Chem.* **141** 235-240 (1998).