| ESRF | **Experiment title: Fast time resolved in-situ powder diffraction experiements: In-situ studies of oxidation/reduction reactions.** | **Experiment number**: 01-02-301 |
|---|---|---|
| **Beamline**: BM01A | **Date of experiment**: from: 9/9 2000 to: 12/9 2000 | **Date of report**: 11/1 2001 |
| **Shifts:** 9 | **Local contact(s)**: Dr. Silvia Capelli | *Received at ESRF:* |


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## Report:

Perovskite materials 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 and Solid Oxide Fuel Cell development and as Colossal Magnetoresistance materials. Interesting properties, such as catalytic activity, magnetic properties and oxygen ion conductivity, are closely related to oxygen stoechiometry, crystal structure and redox properties.

We have used time resolved in-situ powder diffraction to follow oxidation/reduction reactions of oxygen ionconducting perovskite type materials at high temperature, 400-800°C. These materials are of interest in connection with for instance oxygen permeable membranes. The composition of the materials studied were $SrFe_{1-x}Cr_xO_{3-\delta}$ with x=0 and 0.03. The rate of oxidation is dependent on the temperature and the particle size. For the materials studied, the complete reaction is completed in a few seconds at 800°C. Therefor very fast data collection must be used. At the same time, high quality powder diffraction data must be collected in order to be able to follow structural changes during the reaction.

We have developed a Rotating Slit system for the MAR345 imaging plate system at the Swiss/Norwegian beam line, SNBL, which allow data collection with time resolution down to below 0.5 seconds. A steel screen with a wedge-shaped opening is rotated in front af the MAR345 image plate detector. By varying the slit size and the rotation speed, the time resolution for a single rotation can be adjusted.

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

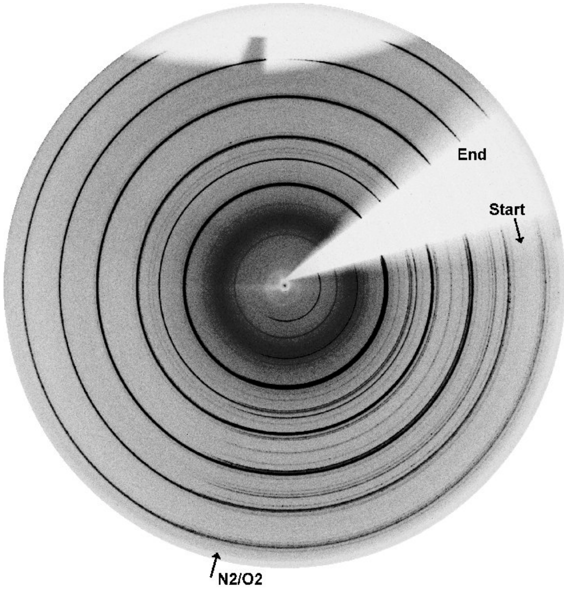


Figure 1

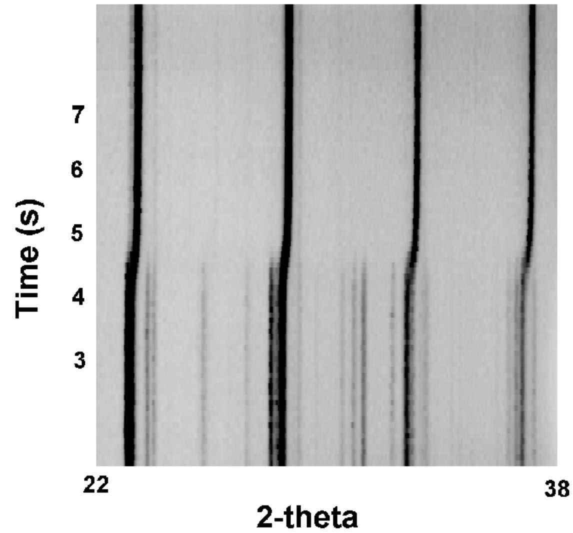


Figure 2

Figure 1 shows an example of an image obtained using the rotating slit setup. The experiment shown is from oxidation of $SrFe_{0.97}Cr_{0.03}O_{2.8}$ at 800°C by switching from nitrogen to oxygen. The slit is rotating continously in front of the imaging plate (one rotation in 15 seconds). The beamshutter is opened, and the gas is switched, marked with an arrow on the Figure. A very fast change in the diffraction pattern is observed. Extraction of time resolved powder diffraction data including correction for polarization effects and conversion to 2θ scale, was performed using FIT2D, using "cake" integration. Figure 2 shows a small part of the extracted powder patterns. The oxidation of the material is accompanied by a very rapid change of symmetry from orthorhombic to cubic, followed by a gradual decrease of the cubic unit cell parameter. As can be seen, the reaction takes place in a few seconds.

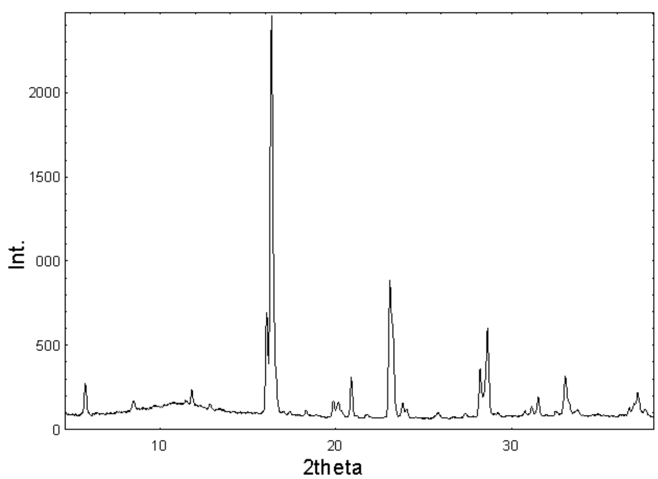


Figure 3

Figure 3 shows an example of a single extracted powder diffraction pattern. The pattern was collected using a 10 deg. slice of the image shown in Figure 1, which is equivalent with an exposure time of ca. 0.5 seconds. As can be seen, the quality of the data are very good. We expect to be able to perform time resolved experiments with time resolution down to ca. 0.1 seconds.