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Time-Resolved Diffraction

In Situ Time-Resolved Neutron Diffraction Investigation during Oxygen Exchange in Layered Cobaltite Cathode Materials**

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The development of in situ techniques for the characterization of solid phases is becoming one of the major issues in current research on materials. This interest relates to the increasing requirement of getting a deeper insight into the changes that occur when a chemical or physical transformation or reaction takes place in the sample under investigation. Time-resolved structural characterization is a valuable tool in this respect, and usually such techniques are used to study the reaction kinetics at a defined reaction temperature,[1–3] mainly by means of X-ray diffraction (XRD). On the other hand, neutron diffraction (ND) is a valuable tool to investigate oxides owing to the sensitivity of neutrons to light atoms such as oxygen and to the possibility of revealing superstructure peaks. Highly studied materials which benefit from the investigation through ND are solid-state ionic (SSI) materials (mainly electrolytes and mixed ionic–electronic materials) for which, for example, the study of oxygen-exchange processes are of great importance to test their performance and define the temperature range for their potential application. To date, to the best of our knowledge, there are no available experimental probes to study the structural evolution of a crystalline solid during oxygen-exchange processes. As the investigated material undergoes a structural change during the diffusion of oxygen into or out of it, it would be highly desirable to develop a method able to simultaneously study the oxygen content variation profile and the structural variation occurring in the sample. This technique could pave the way for extraction of new and essential information on the phenomena occurring during oxygen exchange and can be of relevance for the comprehension of the oxygen migration mechanism and, therefore, could guide the design of optimized compositions.

In view of these relevant applications, we have devised and carried out time-resolved in situ neutron diffraction (ND) measurements under isothermal conditions and with varied oxygen partial pressure $p(O_2)$ inside the measurement apparatus. By recording neutron patterns at proper time intervals it is possible, through the refinement of oxygen occupancies, to determine the concentration profile during oxygen exchange and, at the same time, to have a clear insight into the structural changes occurring in the sample when oxygen is introduced or removed. To our knowledge, our experiment is the first of this kind carried out on any material. Herein we present the result of the experimental work, thus showing the feasibility of this approach to the study of SSI materials and, in general, of any nonstoichiometric oxygen-containing compound. It is clear that this method can also be applied to the in situ time-resolved study of any species that can be easily probed by neutrons, such as hydrogen and deuterium, thus opening new possibilities, for example in the field of hydrogen storage materials.

The compound investigated herein is the $HoBaCo_2O_{5+\delta}$ layered cobaltite. Recently there has been a growing interest in the study of layered cobaltites of general formula REBaCo$_2$O$_{5+\delta}$ (RE = rare earth) owing to their rich structural, electronic, and magnetic phase diagrams, which result from the strong coupling between charge, orbital, and spin degrees of freedom.[4–8] These strongly correlated electron systems have attracted a great deal of attention as a promising alternative to conventional semiconductors in the field of thermoelectric power generation.[9] Moreover, there have been some recent reports suggesting a remarkable oxygen diffusivity in ordered perovskites such as $GdBaCo_2O_{5+\delta}$, which opens a possibility to develop a new class of materials suitable for applications that require a fast oxygen transport in the intermediate temperature range, such as cathode materials in solid-oxide fuel cells (SOFCs).[10] In this respect, Tarancón et al. determined a high oxygen surface exchange and reasonable oxygen ion diffusivity for $GdBaCo_2O_{5+\delta}$ in the temperature range 500 to 700 °C, which suggests the suitability of this mixed ionic–electronic conductor as a cathode material for intermediate-temperature SOFCs.[10] This easy oxygen diffusivity is related to the large oxygen nonstoichiometry found in the layered cobaltites, with δ theoretically varying from 0 to 1, and to the peculiar structural properties of these layered cobaltites.

The $HoBaCo_2O_{5+\delta}$ sample was measured according to the method described in the Experimental Section. Briefly, three temperatures were selected: 573, 673, and 773 K. At each temperature, the sample was equilibrated in either Ar or O_2, and then the gas flux was switched to the other gas (O_2 and Ar, respectively) until the new equilibrium was achieved. ND patterns were acquired every 120 s during oxygen exchange.

From the Rietveld refinement based on the neutron diffraction data it was determined that for all the temperatures investigated, both under argon and oxygen atmospheres, the $HoBaCo_2O_{5+\delta}$ patterns are properly described by considering the tetragonal $P4/mmm$ crystal structure with $a = b = a_p$ and $c \approx 2a_p$, in agreement with previous reports for

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$0 < \delta < 0.50$.[11] Figure 1 shows, as a selected example, the refined pattern of the $HoBaCo_2O_{5+\delta}$ sample at 573 K under Ar.

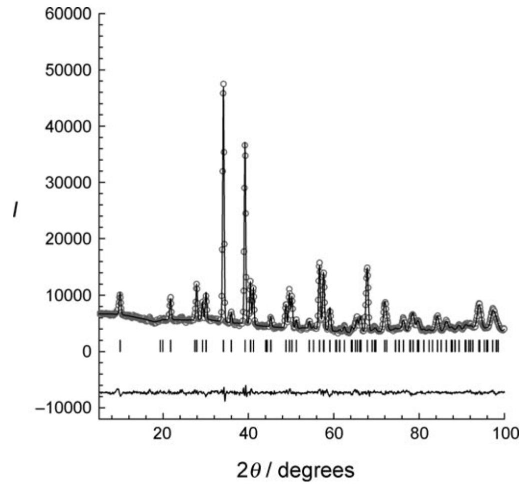

Figure 1. Observed data points and calculated pattern after Rietveld refinement of the $HoBaCo_2O_{5+\delta}$ neutron diffraction pattern at 573 K under Ar. Gray empty circles are the experimental data. The black line is the calculated pattern. The vertical bars at the bottom of the pattern are the Bragg peak positions. The horizontal black line shows the difference between the calculated and experimental patterns.

In the tetragonal structure there are three distinct oxygen sites: O1 located at (0,0,0), O2 at (0,0,0.5) and O3 at (0,0.5,ca 0.301). Figure 2 shows a sketch of the $HoBaCo_2O_{5+\delta}$ structure for $\delta = 0$. The oxygen vacancies are located at the Ho layers (O2 positions, highlighted with an empty square in Figure 2), and along with the increase in the population of the HoO_δ layer, the coordination of the Co ions changes from pyramidal (CoO_5) to octahedral (CoO_6); both coordination modes coexist for $0 < \delta < 1$.

Figure 3 shows the change of the oxygen content for the $HoBaCo_2O_{5+\delta}$ cobaltite as a function of time at 573 K when switching the gas flux from Ar to O_2. The δ value has been determined from the refined occupancies of the O2 site while keeping the O1 and O3 sites fully occupied. The refinement has also been tested in the case of free occupancies for the O1 and O3 sites, and the final result did not show any occupancy change with time for these two sites, thus confirming that the vacancies are only located on the O2 site. The initial oxygen content under argon at 573 K is 5.34(1), while the new equilibrium value under pure oxygen is 5.41(1).

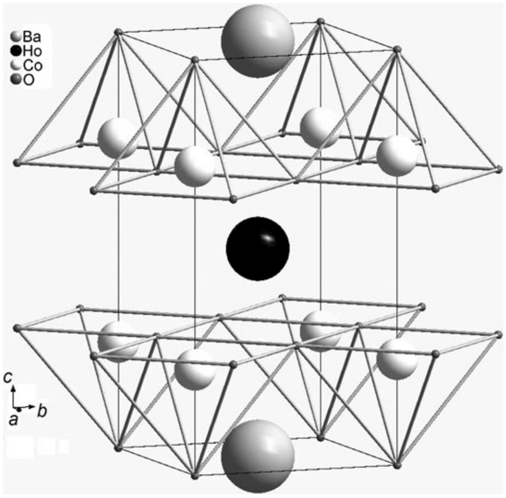

Figure 2. The $HoBaCo_2O_{5+\delta}$ structure for $\delta = 0$.

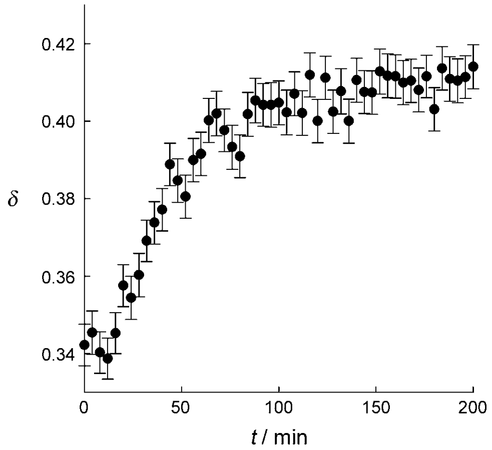

Figure 3. Variation of δ with time in $HoBaCo_2O_{5+\delta}$ at 573 K when the gas flux is switched from Ar to O_2.

In an analogous way to the data shown in Figure 3 (at 573 K), we collected data at 673 and 773 K and refined the corresponding parameters. The values of the equilibrium oxygen content at the three investigated temperatures and under Ar and O_2 fluxes are reported in Table 1.

Table 1: Equilibrium oxygen content of $HoBaCo_2O_{5+\delta}$ as a function of temperature and gas environment.

	573 K	673 K	773 K
argon	5.34(1)	5.26(1)	5.10(1)
oxygen	5.41(1)	5.33(1)	5.21(1)

We will now consider the changes occurring in the cobaltite structure during oxygen exchange. Figure 4 shows the variation of the lattice parameters and cell volume as a function of time for the oxygen insertion at 573 K, selected as a representative example.

The cell volume remains essentially unchanged upon oxygen content exchange, while the *a*(*b*) and *c* lattice parameters show opposite behavior along with the δ increase. The same behavior in the cell parameters is also found at 673 and 773 K. Considering the estimation of the oxygen content provided in the previous paragraph, the data can now be plotted against the equilibrium oxygen content of the samples. We remark that, in contrast to the common procedure of quenching the samples at high temperature once the δ value has been determined (for example by means of thermogravimetry), the data reported herein provide a direct in situ determination of the structural changes occurring during the oxygen content variation and, as a consequence, they

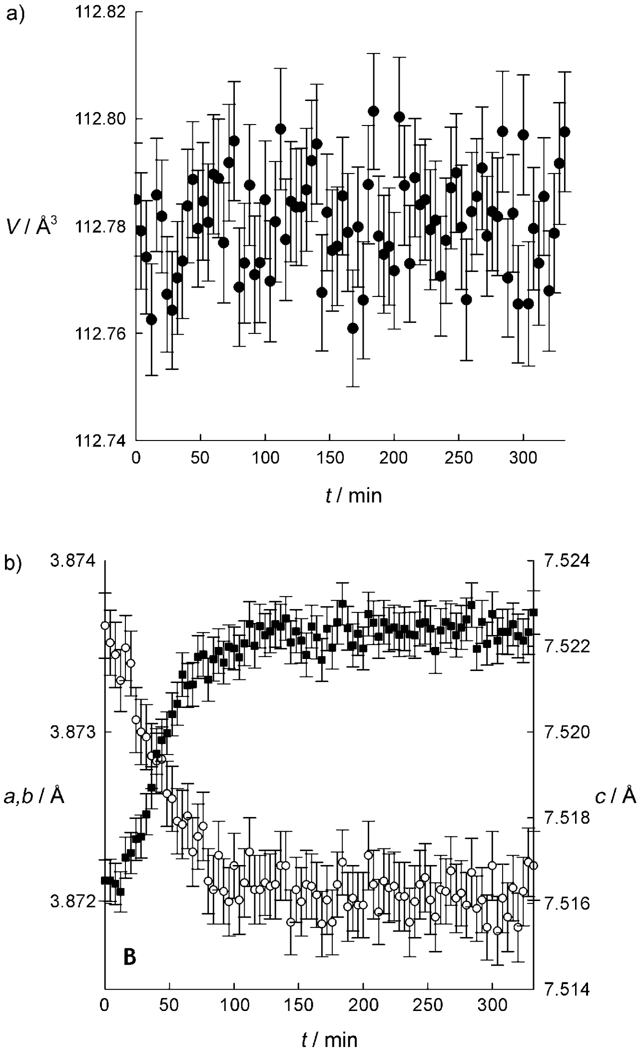

Figure 4. Variation of a) cell volume and b) lattice parameters (empty circles *a*,*b*; full circles *c*) as a function of time during oxygen insertion at 573 K.

represent a reliable parameter to test a material under relevant operational conditions.

Figure 5 presents the overall change of the lattice parameters of the $HoBaCo_2O_{5+\delta}$ cobaltite as a function of oxygen content (calculated by refinement of O occupancies as a function of time) determined in situ at the three selected temperatures. The data have been normalized for the structure expansion associated with the temperature variation. The $a(b)$ parameter linearly decreases when the δ value increases, while the c parameter increases. Overall, the cell volume is essentially constant over the oxygen content range explored herein. This behavior may be due to the compensating effects of cell-size increase arising from the oxygen content increase and the reduction of the radius of the Co ions owing to the oxidation. This unit-cell variation bears witness to a highly anisotropic structural change with oxygen content increase, which is clearly connected to the population of the REO_δ plane and to the increase of the Co–O coordination number from 5 to 6.

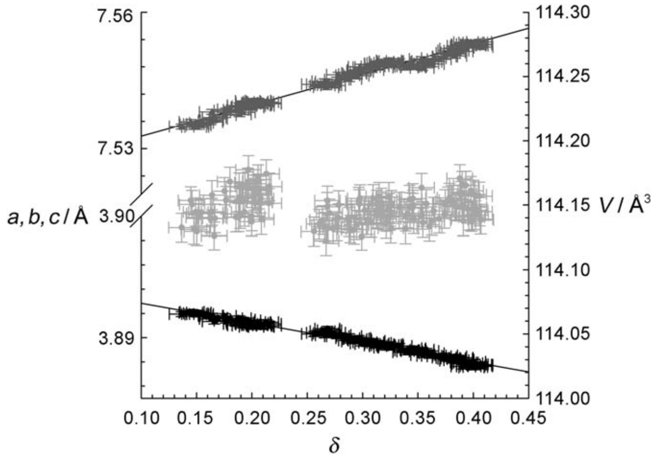

Figure 5. Variation of lattice parameters (*a*,*b* black symbols; *c* dark gray symbols) and cell volume (light gray symbols) as a function of δ for $HoBaCo_2O_{5+\delta}$.

Finally, regarding the atomic positions, in the cobaltite crystal structure the only "free" coordinates are the z Co and z O3 coordinates. For all three temperatures investigated, the z coordinate for Co does not change with δ variation, while the z coordinate for O3 exponentially decreases along with the oxygen content increase of about 0.65–0.7%.

In conclusion, we have presented herein the first time-resolved in situ neutron diffraction experiment aimed at determining the structural changes occurring in the structure of an oxide material during oxygen exchange. The presented experimental approach can be extended to an extremely wide class of materials and opens the possibility to precisely study the structural rearrangements taking place in any gas/solid exchange process that involves species that can be probed by neutrons. Further work is planned to test the applicability of this experimental setup to extract the chemical diffusion coefficients from the relaxation curves of oxygen insertion and extraction.

Experimental Section

A powder sample of $HoBaCo_2O_{5+\delta}$ was prepared by conventional solid-state reaction as reported in reference [11]. Neutron powder diffraction measurements were carried out on a sample put into a sealed quartz sample holder equipped with a gas inlet system connected to certified gas cylinders. The sample was first annealed under argon atmosphere, $p(O_2) = 10^{-6}$ atm, at 573 K and left under these conditions until the equilibrium oxygen content had been achieved (monitored by the evolution of selected diffraction peaks). Once the equilibrium had been reached, the gas flux was suddenly changed from pure argon to pure oxygen, $p(O_2) = 1$ atm, and the diffraction patterns were collected every 120 s at a wavelength of 1.30 Å in the angular range from 5 to 130° on the D20 instrument at the ILL facility (Grenoble, France) using the high-resolution mode. After equilibration to the new oxygen content, the gas flux was switched back to argon. The same procedure was then repeated at 673 and 773 K. Temperature control assured a precision of ±0.5°C. All the neutron diffraction patterns were analyzed according to the Rietveld method using the FULLPROF software package.[12] Cell parameters, atomic positions, and isotropic thermal factors for all the ions were refined. The background arising from the empty quartz tube was recorded at the same temperatures and subtracted from the ND patterns of the samples.

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