In Situ Study of the Reaction Sequence in the Sol–Gel Synthesis of a (Ba0.5Sr0.5)(Co0.8Fe0.2)O3−δ Perovskite by X-Ray Diffraction and Transmission Electron Microscopy

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Examination of the complexing citric acid/EDTA synthesis of (Ba0.5Sr0.5)(Co0.8Fe0.2)O3−δ is presented by in situ X-ray diffraction and transmission electron microscopy, which elucidate all intermediate phases and the formation of the perovskite structure for the first time.

1. Introduction

Mixed ionic-electronic conductors (MIECs) with a perovskite structure are of considerable interest for many industrial processes because they allow the supply or removal of oxygen to or from reaction mixtures with infinite selectivity and high oxygen fluxes. Thus, many applications of MIECs have already been reported, e.g. as cathode material in solid-oxide fuel cells as well as in the production of oxygen-enriched air and increased oxygen fluxes. Thus, many applications of MIECs have already been reported, e.g. as cathode material in solid-oxide fuel cells as well as in the production of oxygen-enriched air and high oxygen permeation performance. Although many reports on this material are already available, a fundamental understanding of the synthesis process and thus the perovskite formation is still lacking. Additionally, investigation of this process is also believed to provide a clarification of the decomposition reaction that takes place in long-term oxygen permeation experiments in membranes of the BSCF material. Already in the year 2000, the decomposition of BSCF into BaCoO2 and Sr(Co1/2Fe1/2)O2−δ was postulated but only due to X-ray diffraction (XRD) measurements of permeated membranes. The appearance of similar additional reflections was described in 2005 in a temperature-programmed XRD pattern of BSCF particularly when the temperature was set below 700°C for 12 h. But no phase attribution was given there.

Because a real understanding of the BSCF formation and decomposition does not exist, we present a detailed study of the synthesis process of BSCF by in situ XRD as well as by transmission electron microscopy (TEM) experiments.

II. Experimental Procedures

The synthesis of BSCF was conducted via a sol–gel route as reported by Shao et al. An aqueous solution containing stoichiometric amounts of the metal nitrates, citric acid, EDTA, and ammonia was stirred at 150°C until a purple-colored gel was obtained. The gel was precalcined at 600°C for 1 h in order to obtain the first crystalline products. XRD measurements were taken with steps of 20 and 25 K, respectively, in order to achieve a high resolution within the temperature dependence. Before each data acquisition, an equilibrium time of 1 h was set. Synthetic air was used as the atmosphere within the chamber. Moreover, an ex situ XRD study has been conducted in order to confirm in situ XRD measurements, to exclude changes in the unit cell dimensions simply due to heating, and as a reference to calculate unit cell parameters. TEM experiments were performed with a powder sample, which was preliminarily heated to 700°C for 1 h, quenched to room temperature, and then glued between silicon single crystals, polished, and finally Ar⁺ sputtered to electron transparency.

III. Results and Discussion

Figure 1 shows the temperature-dependent XRD pattern of the reaction mixture between 400°C and 950°C. Up to 600°C, the reaction mixture consists only of aragonite-type (Ba0.5Sr0.5)CO3 as well as (Co0.4Fe0.6)Co2O4 with spinel modification. At 600°C, two other phases start to form because additional reflections at 26.5°, 32.3°, and 42.5° emerge in the XRD pattern. These reflections are related to a cubic phase with a perovskite structure (perovskite I) and an additional second phase, which is attributed to (Ba0.75Sr0.25)CoO3−δ (hexagonal). In 1977, Taguchi et al. reported on a structure of BaCoO3 that showed almost the same diffraction pattern as the hexagonal phase found here. Therefore, the formation of a similar phase during the process reported here can be assumed. A detailed calculation of the cell dimensions shows a cell parameter that is smaller than that expected for BSCF. Therefore, we postulate a strontium-enriched perovskite phase, namely (Ba0.6Sr0.4)(Co0.6Fe0.4)O3. Further proof for this supposition lies in the systematic shift of the reflections that are related to the hexagonal phase (hexagonal) toward greater angles, indicating a smaller unit cell based on (Ba0.75Sr0.25)CoO3. This has been proved by the synthesis of several compositions within the system (Ba1−xSr0.5CoO3)−δ.

Thus, the reaction of the first crystalline phases can be described as follows:

\[2(Ba_{0.5}Sr_{0.5})CoO_3 + 2/3(Co_{0.4}Fe_{0.6})Co_2O_4 + (4/3−δ)O_2 → (Ba_{0.75}Sr_{0.25})CoO_3−δ + (Ba_{0.25}Sr_{0.75})(Co_{0.6}Fe_{0.4})O_3−δ + 2CO_2\]

On increasing the temperature, one observes a continuous increase of the cell parameter of the perovskite structure (perovskite I) until it reaches the maximum shift at 950°C. This can be concluded as the reflection related to the (110) plane that shifts toward lower angles (see Fig. 1). While the unit cell of the...
perovskite structure increases, a systematic change in the hexagonal structure occurs. From the XRD pattern, it can be seen that the reflection related to the (101) plane of the hexagonal phase shifts toward higher angles. A detailed examination of ex situ XRD measurements further indicates that this shift is not simply due to a further increase of the hexagonal unit cell as reflections related to planes (110) and (201) are shifted differently, which indicates the formation of a different structure. We believe that the change in the hexagonal phase (hexagonal) is due to the intake of strontium and iron ions caused by a gradient in the chemical potentials. This seems to be a logical step due to the incorporation of barium ions into the cubic phase and the cobalt-enriched hexagonal phase. Ex situ XRD patterns indicate a phase transformation toward a tetragonal unit cell (tetragonal), with cell parameters \( a = 5.63 \) Å and \( c = 4.01 \) Å, which is in good agreement with the findings of Yoshiya et al. in 2004.\(^9\) They applied the first principles method to calculate the free energies within the system \( \text{Ba}(\text{Co}_{1-x}\text{Fe}_x)\text{O}_3 \). It has emerged that increasing the iron content lowers the transition temperature from the hexagonal to the above-mentioned tetragonal phase. This tetragonal phase can be regarded as a distorted cubic perovskite structure. The unit cell contains two formula units and reflects a nonideal arrangement of the BO\(_6\) octahedra resulting in a tetragonal structure.

In order to support the XRD findings, TEM experiments were conducted to analyze the microstructural arrangement during the synthesis. Figure 2 shows an STEM bright-field micrograph and corresponding HRTEM micrographs of two grain contacts (Figs. 2(b) and (c)). Quantitative energy-dispersive X-ray analysis (EDXS) of the elemental distribution shows that the selected grain contacts are located between the cubic \( (\text{Ba}_{0.25}\text{Sr}_{0.75})(\text{Co}_{0.6}\text{Fe}_{0.4})\text{O}_3 \) and the hexagonal \( (\text{Ba}_{0.75}\text{Sr}_{0.25})\text{CoO}_3 \). The elemental distributions by EDXS of the cations are displayed in Fig. 3. Figures 4 and 5 present the grain contacts as in Figs. 2(b) and (c) but at higher magnifications. The related diffraction information was created via fast Fourier transformation of the HRTEM micrographs. The first grain contact (Fig. 4) is identified to be between a grain with a perovskite structure (perovskite I) and a grain with a hexagonal structure (hexagonal).

The combination of the diffraction information given by the HRTEM with the elemental distribution of these two grains underlines the XRD findings that indicated the coexistence of a perovskite phase with a comparable high strontium amount and a hexagonal structure with a high barium amount. The second
contact (Fig. 5) even exhibits the contact zone between two grains with the above-mentioned stoichiometries. Contrary to the above-described contact between the perovskite and hexagonal phases, the contact in Fig. 5 is identified to separate a grain with tetragonal modification and a second grain with perovskite. As mentioned above, a phase transition of the hexagonal to a tetragonal modification is observed. Thus, this particular grain contact exhibits a contact zone between a former hexagonal phase in which the postulated phase transition to the tetragonal modification has taken place. A closer look at the diffraction data shows that these grains are not randomly oriented but have parallel zone axes as \([1,0,0]_c∥[1,1,1]_t\) and parallel planes as \((1,1,0)_c∥(0,1,0)_t\). This finding gives rise to the assumption that a reaction has occurred between these two grains and is underlining the fact that during uptake of strontium and iron ions into the hexagonal structure, a phase transition to a tetragonal structure occurs.

When the temperature was increased further, reflections for perovskite I shifted to lower angles (larger unit cell), which is due to the further uptake of barium ions. Additionally, the reflection for plane \((101)\) of the tetragonal phase diminished, which was clearly due to an increase of symmetry, and ended up in a cubic perovskite structure. Thus, the first reaction is followed by transformation of the hexagonal into the tetragonal phase and the final formation of the perovskite; while the reaction process is a dynamic rather than a static process, the stoichiometry of the reactants vary within a certain tolerance.

\[
\begin{align*}
&h-(\text{Ba}_{0.75}\text{Sr}_{0.25})\text{CoO}_3_{-\delta} + c-(\text{Ba}_{0.25}\text{Sr}_{0.75})\text{(Co}_{0.6}\text{Fe}_{0.4})\text{O}_3_{-\delta} \\
&\rightarrow t-(\text{Ba}_{0.6}\text{Sr}_{0.4})\text{(Co}_{0.6}\text{Fe}_{0.4})\text{O}_3_{-\delta} + c-(\text{Ba}_{0.4}\text{Sr}_{0.6})\text{(Co}_{0.8}\text{Fe}_{0.2})\text{O}_3_{-\delta} \\
&\rightarrow 2c-(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{(Co}_{0.8}\text{Fe}_{0.2})\text{O}_3_{-\delta}
\end{align*}
\]

It has to be emphasized that the formation of the final cubic BSCF perovskite (perovskite II) takes place in both the tetragonal (former hexagonal) lattice and the cubic perovskite system (perovskite I) with a smaller unit cell. If the BSCF structure would only grow at the expense of the cubic phase by incorporation of barium ions, one would expect a simple diminution of the hexagonal barium-rich phase. As shown, in fact, a phase
Fig. 5. HRTEM micrograph of grain contact shown in Fig. 2(c). Diffraction data taken via fast Fourier-transformation from selected areas (b-d).

Fig. 6. Scheme of the relationship between hexagonal and cubic perovskite structures visualized by the stacking sequence of the hexagonal layers of barium and oxygen ions (gray ball, oxygen; white, barium; black, cobalt).
transition of the hexagonal to a tetragonal structure occurs. The oxide with a hexagonal structure is strongly related to the cubic perovskite structure. Both the cubic perovskite as well as the hexagonal oxide can be understood as close-packed hexagonal layers of barium (strontium) and oxide ions that are stacked in the hexagonal close packing in the first and in the cubic close packing in the second. While the CoO₆ octahedra share faces in the first place, only corner-sharing (Co,Fe)O₆ octahedra are eminent in the second place. Thus, it seems likely that the final perovskite is formed in both the hexagonal—via the formation of the tetragonal unit cell—and in the cubic system by a simple substitution of strontium by barium in the lattice, leading to a larger unit cell.

Figure 6 schematically displays the relation between the hexagonal and the cubic perovskite structure. The stacking sequence in the hexagonal cell is ABABABAB—containing just face-sharing octahedra—while the stacking sequence in the perovskite structure is ABCABCAB—containing just corner-sharing octahedra. The existence of fairly distorted close-packed layers in the hexagonal structure is the reason for the occurrence of an intermediate tetragonal phase, which can be understood simply as a distorted perovskite structure explained above.

Obviously, the last reaction of the above-presented reaction sequence is a reversible process that becomes more favorable at temperatures significantly higher than 800°C. This explains the fast decomposition of BSCF below 800°C.

IV. Summary

The synthesis process of BSCF via the commonly applied sol–gel method has been studied in considerable detail. First crystalline intermediates have been identified as a mixed carbonate and a mixed spinel. Second, two mixed oxides are formed: one with a hexagonal structure and one with a cubic structure. Both structures are related to the structure of the cubic BSCF and it was shown that the cubic perovskite structure is finally formed at the expense of both the hexagonal phase—via a tetragonal phase—and the cubic structure.

References