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Electron microscopy study of Yttrium-doped $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$

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ABO_3-type perovskite oxides have been identified as promising materials for application in oxygen separation membranes. Among these perovskites $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) has received particular attention due to its exceptional high oxygen permeation properties. However, a major obstacle for the application is the thermodynamic instability of the cubic BSCF phase at application-relevant temperatures. The desired cubic phase decomposes at temperatures below 900 ^{o}C, resulting in a slow decrease of oxygen flux making it unsuitable for long-term operation. It is assumed that the decomposition is initiated by the decreasing concentration of oxygen vacancies with decreasing temperature which requires an increase of the valence of the B-site cations to preserve overall charge neutrality. This leads to a change of the ionic radius of the B-site cations and a corresponding destabilization of the cubic BSCF phase. Therefore, the cubic phase decomposes into various secondary phases, like the hexagonal BSCF phase, Co-oxide, precipitates with plate-like morphology, which are composed of thin lamellae of the cubic and hexagonal phases, and barium cobaltites $Ba_{n+1}Co_nO_{3n+3}(Co_8O_8)$ with $n \geq 2$ (denoted BCO) [1-4].

To improve the long-term stability of the cubic BSCF phase B-site doping with monovalent transition metals was investigated. Recent studies show improved phase stability for Zr-doped BSCF with a dopant concentration as low as 3 at% [5]. Furthermore, Y-doped BSCF has been reported to even improve considerably the oxygen conductivity [6]. However, a detailed phase investigation with high spatial resolution is still missing. Therefore, undoped and Y-doped BSCF was investigated by transmission electron microscopy and scanning electron microscopy (SEM). Electron energy loss spectroscopy (EELS) was applied to study the valence of the Co-cations. Energy dispersive X-ray spectroscopy (EDXS) was used for composition analysis.

Y-doped BSCF powder was prepared using the mixed-oxide route. Mixed raw powders were calcined and isostatically pressed into compacts. After sintering and homogenization, the bulk samples were annealed at temperatures from 700 ^{o}C to 900 ^{o}C for 100 h in ambient air. Prior to the SEM investigation the bulk samples were polished up to a surface roughness of about 0.1 µm, followed by an etching process using a colloidal silicon dioxide suspension. Due to the different etching rates of the different BSCF phases, a surface topography develops resulting in secondary electron contrast. This contrast can be directly related to the different BSCF phases [3], which allows a quick large-scale characterization of the phase composition of numerous samples.

Figure 1 shows SEM images of etched (a) undoped and (b) 3 at% Y-doped BSCF bulk samples after annealing at 700 ^{o}C. Undoped BSCF contains a large volume fraction of secondary phases, mainly precipitates with plate-like morphology surrounded by the hexagonal phase with dark contrast as shown in Fig. 1(a). Furthermore, CoO precipitates could be observed. In contrast, Y-doped BSCF only shows the hexagonal phase which can be found exclusively at grain boundary regions (dark contrast in Fig. 1(b)). After 800 ^{o}C annealing, the hexagonal phase is only formed at triple points of grain boundaries in Y-doped BSCF. At 900 ^{o}C, secondary phases were not detected in Y-doped BSCF whereas undoped BSCF contains BCO-type lamellae and CoO grains. Therefore, Y strongly reduces the concentration of nucleation centers for the hexagonal phase compared to undoped BSCF.
However, Y does not fully suppress the formation of the hexagonal phase. Therefore, chemical analyses were performed to gain further insights into the decomposition process. EDXS mappings of a region containing the cubic BSCF phase and the hexagonal phase at a grain boundary (Figure 2) show a strong increase of Co and a depletion of Fe and Y whereas the Ba- and Sr-concentrations (mappings not shown here) only change marginally. The lack of Y in the hexagonal phase might be one reason for the improved phase stability because the formation of secondary phases requires a strong diffusion of B-site cations which might be suppressed by the large ionic radius of Y^{3+}.

Since the change of the Co-valence plays a major role in the decomposition process, the Co-valence state was investigated by EELS. Since the Ba-$M_{4,5}$ white-lines are superimposed on the Co-

$L_{2,3}$ white-lines, Co-valence determination cannot be performed by the measurement of the Co-$L_{2,3}$ white-line intensity ratio. Therefore, a new method was developed to characterize the Co-valence state in BSCF by determining the change in Co-$L_{2,3}$ white-line distance. This technique was elaborated on the basis of Co-$L_{2,3}$ white-line distance measurements of reference materials with known Co-valence state. This method allows to easily map the Co-valence over a comparably large region as shown in Figure 3(a). The corresponding sample area of the mapping is marked with a white frame in the HAADF-STEM image Figure 3(b). Figure 3(a) confirms the supposed different Co-valence states in the hexagonal and cubic phase. In the cubic phase of Y-doped BSCF the valence of cobalt is about 2+, whereas in the hexagonal phase the valence state of cobalt is elevated (≥2.6+).

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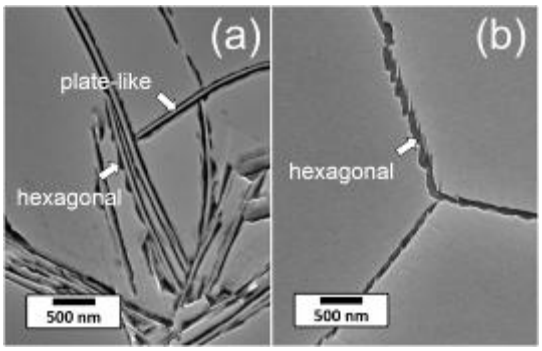

Figure 1. SEM micrographs of etched (a) undoped and (b) 3 at% Y-doped BSCF annealed at 700 ^{o}C for 100 h. The dark contrast corresponds to the hexagonal phase.

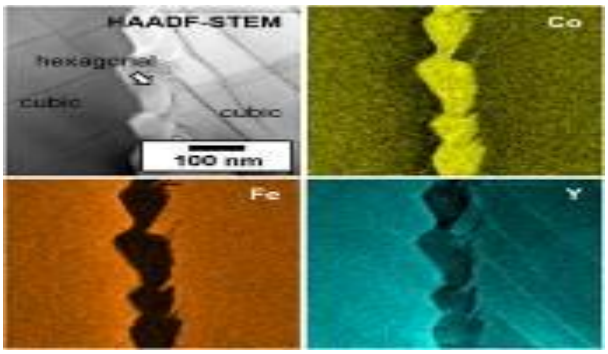

Figure 2. EDXS mappings of the Co-, Y- and Fe-distribution in cubic BSCF and hexagonal BSCF at a grain boundary in 3 at% Y-doped BSCF annealed at 700 ^{o}C for 100 h.

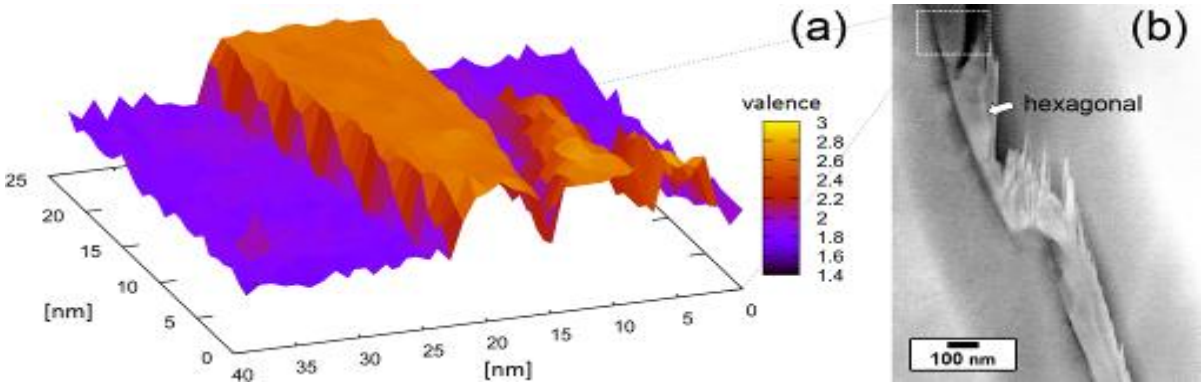

Figure 3. (a) EELS Co-valence mapping of a grain boundary region containing the hexagonal phase in 3 at% Y-doped BSCF annealed at 730 ^{o}C for 100 h. (b) Overview HAADF-STEM image. The white frame corresponds to the sample area where the Co-valence mapping was performed.