Karlsruhe Institute of Technology

Laboratory for Electron Microscopy

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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Introduction

- $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) in the cubic phase promising mixed ionic and electronic conducting perovskite (Fig. 1)
- Application in future CO_2-emission free power plants as oxygen separation membrane (Fig. 2)
- Highest oxygen conductivity at application relevant temperatures (700 … 900 °C)
- However, *fast degradation and poor long time stability at temperatures below 900 °C* by secondary phase formation (hexagonal BSCF, CoO, „plate-like“ precipitates [1,2] consisting of lamellae of different phases (cubic, hexagonal and Ba-cobaltate)
  induced by temperature-dependent change of O-concentration and corresponding change of Co-valence state
- Improvement of conductivity and stability through B-site doping with monovalent transition metals [3, 4]

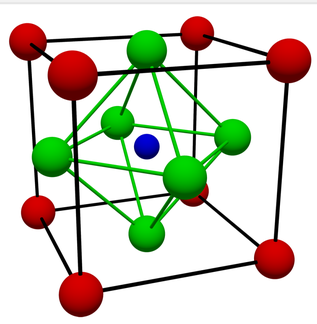

Fig. 1: ABO_3 perovskite structure

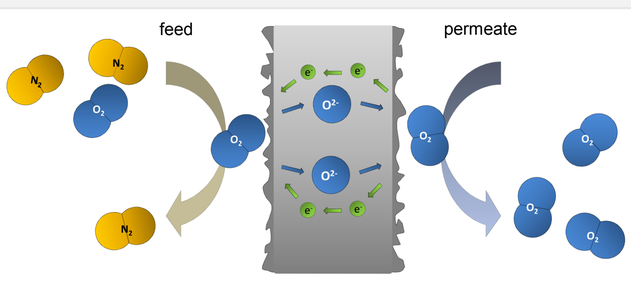

Fig. 2: Oxygen separation membrane

- **S**canning **e**lectron **m**icroscopy (SEM) and additional **T**ransmission **e**lectron **m**icroscopy (TEM) investigations reveal decomposition process and phase stability

Fabrication

- Calcination of powder by mixed oxide route
- Dopant concentration: 0 – 10 at% Y on B-site
- Isostatic pressing at 250 MPa into ceramic compacts
- Sintering at 1100 °C for 12 h and homogenization at 1000 °C for 24 h
- Annealing in air at 700 – 900 °C for 100 h and quenching in water

Sample preparation

SEM sample preparation and phase mapping

- Polishing by diamond lapping film
- Chemical etching using colloidal silicon (Fig. 3)
- SEM imaging in ZEISS LEO 1530 Gemini and FEI Quanta 650 ESEM

Fig. 3: Scheme of chemical etching process

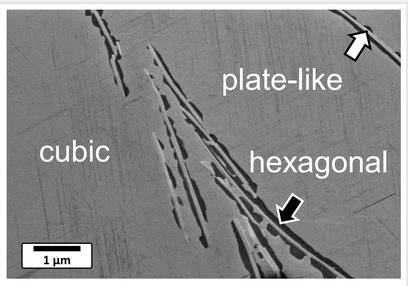

Fig. 4: SEM image of chemically etched BSCF bulk

➡ Contrast due to topography
➡ Mapping of different phases by SEM imaging [1] (Fig. 4)

TEM, STEM, EDXS and EELS

- Standard TEM sample preparation by embedding in ceramic cylinder, dimple grinding, Ar^+-ion milling
- Microscopes: Philips CM 200 FEG/ST and FEI Titan^3 80-300

Experimental Results

Microstructure

Yttrium doping suppresses

- CoO precipitates
- Plate-like phase at doping concentrations ≥ 3 at% (Fig. 5)
  ➡ No secondary phases at T ≥ 900 °C

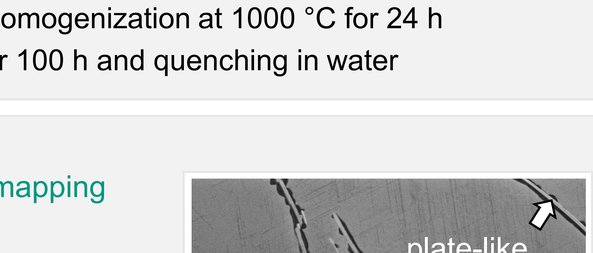

Fig. 5: SEM image of undoped, 1 at% and 3 at% Y doped BSCF annealed at 900 °C for 100 h

- Formation of hexagonal phase at grain boundary triple points (Fig. 5)
- Increasing decoration of grain boundaries at lower temperatures (T < 800 °C)

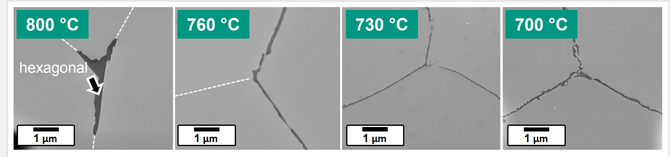

Fig. 6: SEM images of hexagonal phase at different annealing temperatures of 3 at% Y-doped BSCF

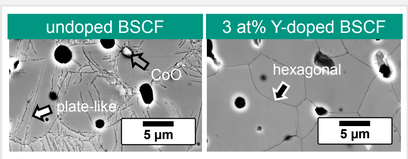

Fig. 7: SEM images of doped and undoped BSCF annealed at 700 °C for 100 h

But: Significant reduction of volume fraction of secondary phases (Fig. 7)

- Hexagonal phase Co-rich, Fe- and Y-depleted (Fig. 8)
- Minor deviation in Ba- and Sr-concentration

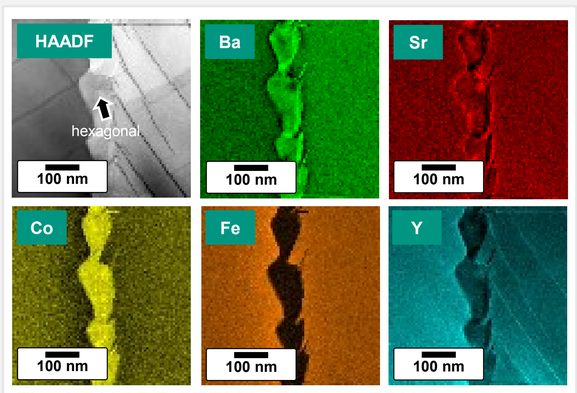

Fig. 8: HAADF-STEM image and EDXS mapping of 3 at% Y doped BSCF annealed at 700 °C

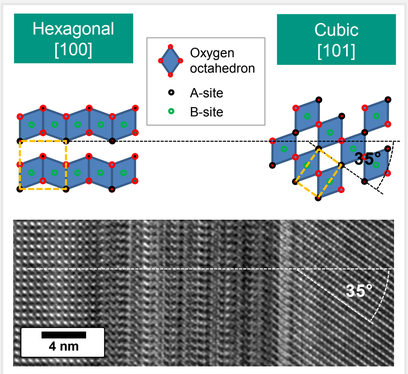

Fig. 9: HRTEM image of interface region between hexagonal and cubic phase

- Orientation relationship between cubic and hexagonal phase
  ➡ Configuration change of oxygen octahedrons from corner-sharing (cubic) to face-sharing (hexagonal) (Fig. 9)
- Complex arrangement of lamellae consisting of cubic and hexagonal phase at interface region (Fig. 9)

Co-valence determination in the cubic and hexagonal BSCF phase

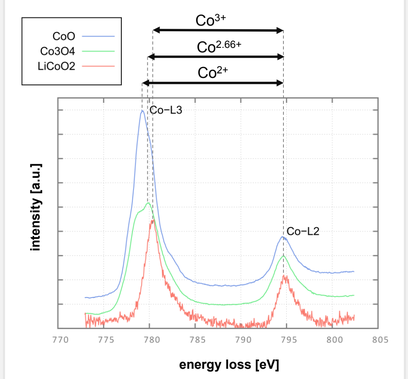

Fig. 10: Reference EELS spectra

- Correlation between Co-L_2/L_3 white-line distance and valence according to reference samples with known Co-valence (Fig. 10)
- Noise reduction of spectra by principle component analysis
  ➡ *Fast valence-state mapping of BSCF on the basis of L_2/L_3 white-line distance*
- Change of average valence from 2.0 ± 0.3 (cubic BSCF) to 2.6 ± 0.3 (hexagonal BSCF) (Fig. 11)

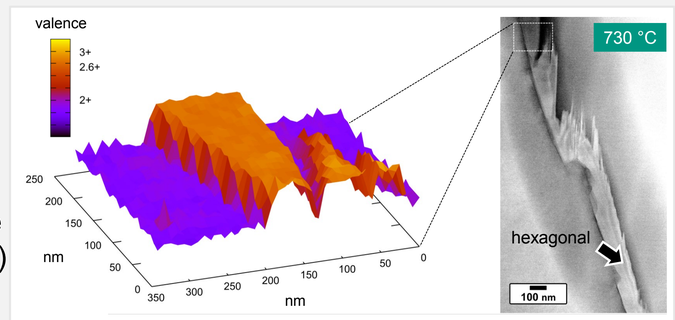

Fig. 11: Co-valence mapping of 3 at% Y-doped BSCF

Summary

- Y-doping suppresses plate-like phase and CoO precipitates (Fig. 12) and confines hexagonal phase to grain boundaries
- New fast EELS-based technique for Co-valence state mapping by correlation of Co-L_2/L_3 white-line distance and Co-valence state for valences between 2+ and 3+

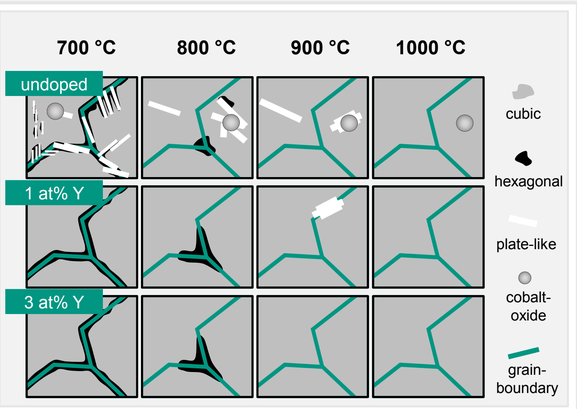

Fig. 12: Schematics of microstructure

References

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Acknowledgement

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