

Decomposition process of a high-performance perovskite at intermediate temperatures studied by analytical TEM

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The cubic perovskite $(\text{Ba}_{0.5}\text{Sr}_{0.5})(\text{Co}_{0.8}\text{Fe}_{0.2})\text{O}_{3-\delta}$ (denoted BSCF) is the state-of-the-art ceramic membrane material for oxygen separation technologies above 900°C. BSCF is a mixed oxygen-ion and electron conductor (MIEC) and exhibits one of the highest oxygen permeabilities reported so far for dense oxides combined with excellent phase stability above 900°C [1,2]. In the intermediate temperature range (500° - 800°C), however, BSCF suffers from a slow decomposition of the cubic perovskite into variants with hexagonal stacking which is a barrier for oxygen transport [3,4]. Different transmission electron microscope techniques as selected area electron diffraction (SAED), high-resolution transmission electron microscopy (HRTEM), high-angle annular dark-field (HAADF), energy-dispersive X-ray spectroscopy (EDXS), and electron energy-loss spectroscopy (EELS) were applied to quenched specimen to elucidate details of the decomposition process. The non-cubic perovskites grow as lamella in a quasi-topotactic manner on (111) planes of the cubic BSCF, and they are enriched in barium and cobalt compared to BSCF. Local composition varies over the lamella and is related to the stacking scheme (see Figs. 1 and 2).

Transition states of the non-cubic perovskites in this dynamic process can be regarded as polytypes with sequences of alternating cubic and hexagonal stacking. However, distortions from ideal symmetry are present. An accompanied in situ high-resolution EELS study with monochromised electrons upon heating of BSCF from room temperature to 950°C regards the cobalt-L_{2,3} (see Fig. 3), iron-L_{2,3}, and oxygen K-edges [5]. Temperature-dependent valence determinations of cobalt and iron were made, and covalent mixing effects of transition-metal:3d orbitals with oxygen:2p orbitals were revealed. The investigations hint to a spin-state transition of trivalent cobalt which yields - at intermediate temperatures - an unsuitable small ionic radius to support a cubic structure, and it is made responsible for the slow decomposition. Concepts for the development of perovskite MIECs with improved stability in the intermediate temperature range are discussed.

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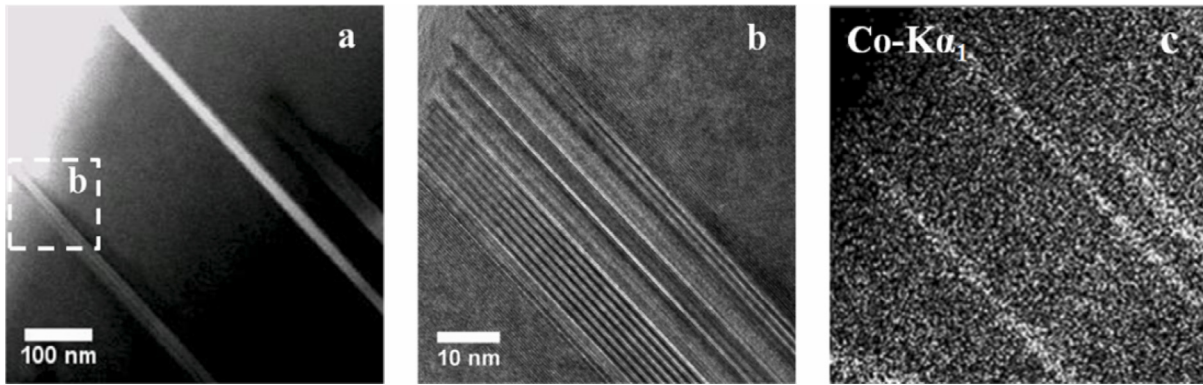


Figure 1. a) STEM bright field of BSCF ceramic after long-term heat treatment at 750°C. b) HRTEM of quasi-topotactically oriented lamella. c) Cobalt distribution by EDXS.

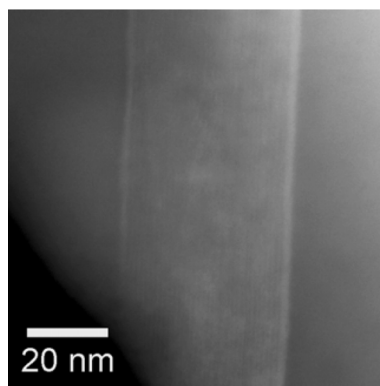


Figure 2. STEM annular dark-field micrograph of lamella in BSCF ceramic showing distribution of barium by bright contrast.

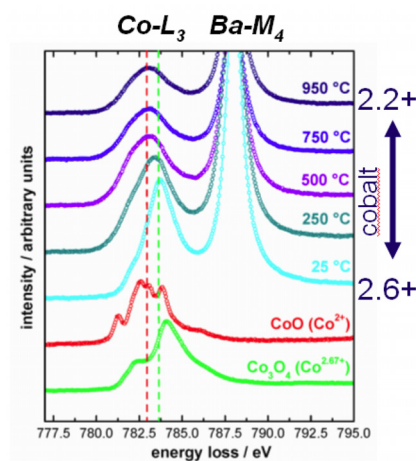


Figure 3. Temperature-dependent high-resolution EEL spectra of BSCF compared to room temperature spectra of oxides with cobalt in known valence state.