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In Situ Electron Energy-Loss Spectroscopy of Cobalt and Iron Valences in a Mixed Conducting Perovskite and the Correlation to a Phase Decomposition at Intermediate Temperatures

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The cubic perovskite $(Ba_{0.5}Sr_{0.5})(Co_{0.8}Fe_{0.2})O_{3-\delta}$ (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.

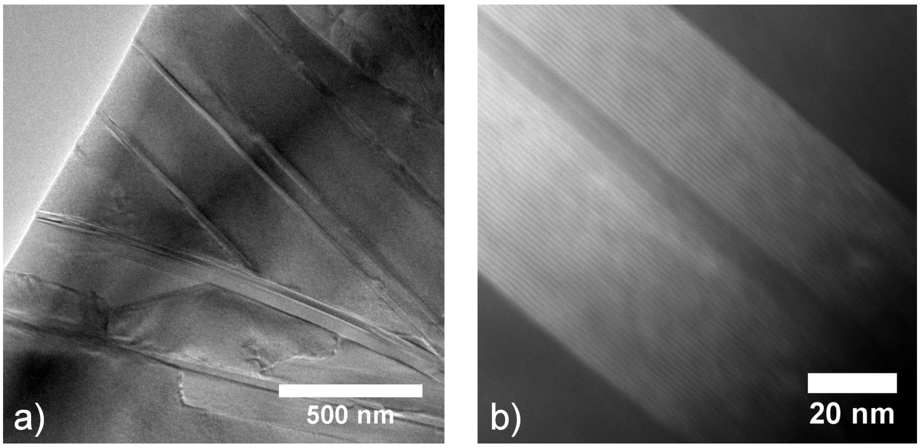

Fig. 1 BSCF ceramic after long-term heat treatment at 750 °C. a) TEM bright-field showing different lamellae, b) STEM annular dark-field micrograph of lamella showing the distribution of barium by bright contrast.

The non-cubic perovskites grow as lamella in a quasi-topotactic manner on different planes of the cubic BSCF (see Fig. 1a), and they are enriched in barium and cobalt as compared to BSCF [4]. Local compositions vary over the lamella and are related to the stacking scheme (see Fig. 1b).

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 accompaning *in situ* high-resolution EELS study with monochromized electrons upon heating of BSCF from room temperature to 950 °C regards the cobalt-$L_{2,3}$ (see Fig. 2), iron-$L_{2,3}$, and oxygen K-edges [5].

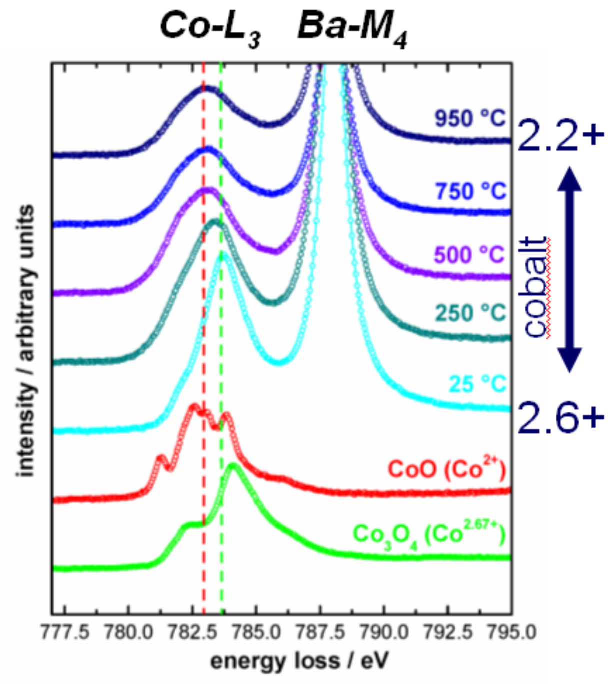

Fig. 2 Temperature-dependent high-resolution EEL spectra of Co-L_3 and Ba-M_4 ionization edges in BSCF compared to room temperature Co-L_3 spectra of oxides with cobalt in known valence state.

Temperature-dependent valence determinations of cobalt and iron were made, and covalent mixing effects of transion-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. These investigations enable the finding of concepts for the development of perovskite MIECs with improved stability in the intermediate temperature range.

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