

A HIGH-TEMPERATURE MÖSSBAUER STUDY INTO IONIC AND ELECTRONIC DISORDER IN BSCF5582

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Perovskite-type compounds of the $(\text{Ba}_{1-x}\text{Sr}_x)(\text{Co}_{1-y}\text{Fe}_y)\text{O}_{3-\delta}$ family have been intensely investigated in respect to their mixed ionic-electronic conductivity and their oxygen disorder which is characterized by extremely high δ -values. The latter properties have made $(\text{Ba}_{0.5}\text{Sr}_{0.5})(\text{Co}_{0.8}\text{Fe}_{0.08}\text{Fe}_{0.12})\text{O}_{3-\delta}$ (BSCF5582) one of the most promising ceramic materials for oxygen separation membranes. We report on ^{57}Fe Mössbauer *in situ* studies of BSCF5582 conducted between room temperature and 1000 °C in atmospheres of variable oxygen activity in order to obtain insight into local coordination and valence of iron at working conditions and into the distribution of oxygen vacancies on their different sites. The magnetically-split room-temperature Mössbauer spectra of BSCF5582 reveal the presence of two inequivalent iron species and show significant changes with oxygen content [1]. Evaluation of signal intensities confirms results from theoretical computations on vacancy formation in BSCF which indicate that formation energies of the various types of oxygen vacancies differ by the order of 0.1 eV only [2,3]. The spectral analysis also shows that the distribution of oxygen vacancies on the different sites of the perovskite structure of BSCF is far from random [1]. In the paramagnetic high-temperature phase ($T \geq 320$ °C), the quadrupole-split signals demonstrate that local symmetry is lower than cubic. At 700, 850, and 1000°C, the spectra have been collected as a function of oxygen activity, a_{O_2} ($5 \cdot 10^{-5} \leq a_{\text{O}_2} \leq 1$). Isomer shifts (IS) as well as quadrupole splittings (QS) were found almost independent of a_{O_2} . This unexpected finding is discussed in respect to simultaneous, stoichiometry-related changes in valence and local coordination of the iron probes. The isothermal decrease of signal intensity observed with increasing oxygen deficit is attributed to changes in the vibrational properties of the highly oxygen-deficient material.

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