

Valence and spin state of iron in aluminum-doped perovskite ceramics

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Perovskite-type oxides of the composition ABO_3 can host many different cations on the A- and B-sites, which enables us to tune conductivities from almost pure electronic to almost pure ionic. Membranes with both high flux and selectivity are based on mixed ionic-electronic conductors (MIECs) with perovskite structure [1,2]. Due to their multiple applications, new perovskite materials are of major interest for natural scientists, like chemists and materials scientists.

This abstract presents novel cobalt-free perovskite materials of $A^{II}B^{III/IV}O_{3-\delta}$ - type, containing iron and aluminum with the stoichiometries $(Ba_{0.5}Sr_{0.5})(Fe_{1-x}Al_x)O_{3-\delta}$ (BSFA). Doping of the B-site of the perovskite structure with a metal with a fixed valence state, like the trivalent aluminum, is expected to lead to the diminution of non-stoichiometric oxygen variations and a more stable redox behavior of the material. Electron energy-loss spectroscopy (EELS) and Mössbauer spectroscopy revealed the iron oxidation and spin-states and the hybridization of iron and oxygen. In order to investigate the electronic structure, the iron $L_{2,3}$ - (Figure 1a) and oxygen K-edge (Figure 1b) were examined by EELS measurements. The iron $L_{2,3}$ -edge displays an electronic transition from the Fe-2p core orbitals to the partly unoccupied Fe-3d orbitals (energetic location displayed schematically in [3]). The validity of the dipole elective rule in principle attributes the sensitivity of this measurement to the chemical environment of iron with respect to coordination, valence and spin configuration [4]. Figure 1a shows no significant changes of the overall shape and position of the iron $L_{2,3}$ -edge for the different BSFA samples. However, compared to standards for Fe^{4+} ($SrFeO_3$) and Fe^{3+} ($\alpha-Fe_2O_3$) all BSFA samples show a smaller FWHM of the L_3 white line. That indicates a mixed valence of Fe^{3+}/Fe^{4+} and a small energy difference between the intra-atomic exchange splitting and the cubic crystal field splitting, making a competition of iron high-spin and low-spin states likely. The presence of Fe^{2+} or Fe^{6+} can be excluded. The oxygen K-edge is caused by the transition of oxygen 1s orbitals into orbitals with oxygen 2p character. If the iron 3d orbitals are hybridized with the oxygen 2p ligand orbitals, the energy-loss near-edge structure of the oxygen K-edge also reflects the occupation of the iron 3d orbitals. That means the charge distribution between oxygen and iron is reflected in both the iron $L_{2,3}$ -edge and the oxygen K-edge [5]. Figure 1b displays the oxygen K-edge, which is separated into three parts: the low energy part A (525-532 eV), reflecting the hybridization of the oxygen 2p orbitals with the partly occupied iron 3d orbitals; a middle energy part B (532-547 eV), reflecting the hybridization of the oxygen 2p orbitals with the barium 4f, strontium 4d and aluminum 3p orbitals; and the high energy part C (above 547 eV), reflecting the hybridization with the empty iron 4sp band [3,6,7]. The occurrence of the A peak of the O K-edge leads to the conclusion that there is a significant amount of covalency due to the iron 3d–oxygen 2p

hybridization. As the formal valence of iron decreases, the occupation of the hybridized 3d orbitals with the oxygen 2p ligand is diminished. Therefore, the probability of exciting a core electron into these orbitals is lower. This is reflected in the peak area [8,9] The intensity ratio B/A follows from estimating the integral intensities in the energy-loss intervals 532-547 eV and 525-532 eV. It increases from 4.55 (BSF) to 5.26 (BSFA0.1). Thus, the hybridization of Fe-3d with O-2p decreases slightly relatively to that of the other cations (Ba-4f, Sr-4d, Al-3p). Obviously aluminum takes part in the charge transfer, and thus, the covalent mixing of iron and oxygen orbitals decreases, leading to the extension of the lattice with increasing aluminum content.

EELS revealed a significant amount of covalency by Fe-3d–O-2p hybridization and a mixed Fe³⁺/Fe⁴⁺ valence state of iron for all synthesized perovskites, which was quantified by Mössbauer spectroscopy. Trivalent aluminum replaces a higher fraction of Fe⁴⁺ than of Fe³⁺ while both iron species are in high-spin state. Fe⁴⁺ is predominantly substituted by Al³⁺ due to their similar ionic radii, but with this substitution the oxygen deficit has to be increased. This results in a higher oxygen vacancy concentration. Due to an improved long-time stability preserved by a less flexible redox behavior and a stable high-spin configuration of iron, a good performance in the intermediate temperature range, where cobalt containing perovskites have serious stability problems, is expected in application.

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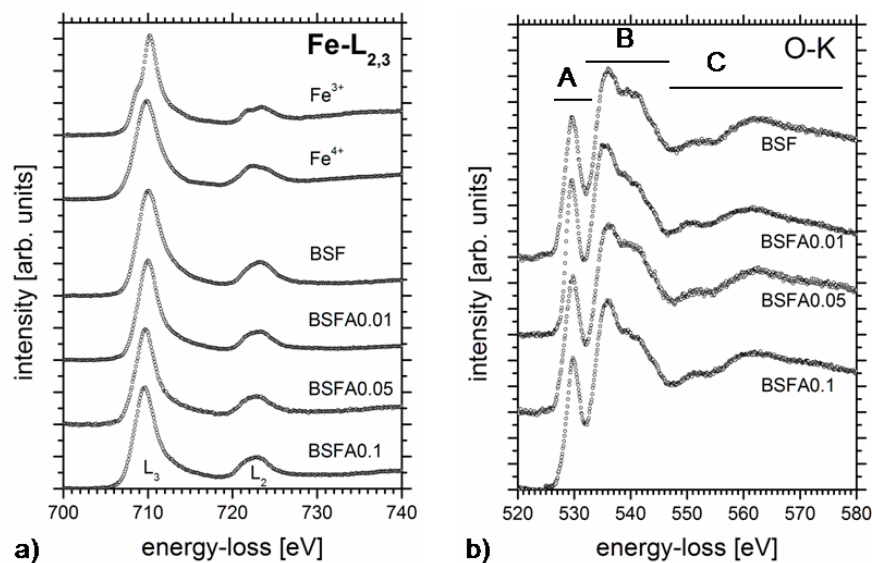


Figure 1. Room-temperature EEL spectra a) of the Fe-L_{2,3} edge for BSF, BSFA0.01, BSFA0.05, and BSFA0.1 compared to Fe³⁺ and Fe⁴⁺ standards, b) of the O-K edge for BSF, BSFA0.01, BSFA0.05, and BSFA0.1.