Spin-state transition of iron in (Ba$_{0.5}$Sr$_{0.5}$)(Fe$_{0.8}$Zn$_{0.2}$)O$_{3-\delta}$ perovskite

Armin Feldhoff$^{a,*}$, Julia Martynczuk$^{a,1}$, Mirko Arnold$^a$, Maxym Myndyk$^b$, Ingo Bergmann$^{b,2}$, Vladimir Šepelák$^{b,3,4}$, Wolfgang Gruner$^c$, Ulrich Vogt$^d$, Angelika Hähnel$^e$, Jörg Woltersdorf$^e$

$^a$ Institut für Physikalische Chemie und Elektrochemie, Leibniz Universität Hannover, D-30167 Hannover, Germany
$^b$ Institut für Physikalische und Theoretische Chemie, Technische Universität Braunschweig, D-38104 Braunschweig, Germany
$^c$ Leibniz-Institut für Festkörper- und Werkstoffforschung Dresden, D-01069 Dresden, Germany
$^d$ EMPA, Materials Science & Technology, CH-8600 Dübendorf, Switzerland
$^e$ Max-Planck-Institut für Mikrostrukturphysik, D-06120 Halle, Germany

1. Introduction

Ceramic membranes can provide remarkable oxygen permeation fluxes at infinite selectivity without the need of external electrodes when they are based on heavily doped anion deficient cubic perovskite-type $\text{A}_x\text{B_x\text{O}_6}$ oxides exhibiting mixed oxygen-ion and electron conductivities at elevated temperatures (500–1000 °C) [1]. While the partial conductivity of electrons is distinctly higher than that of oxygen ions [1,2], the oxygen deficit $\delta$ correlates directly with the obtainable permeation flux via the concentration of disordered oxygen vacancies. The perovskite lattice can tolerate a remarkable number of vacant oxygen sites if a reducible transition metal cation is located at the crystallographic B site in the center of the BO$_6$ octahedron. Upon heating under constant pressure, entropy may free up even more oxygen from a previously equilibrated perovskite. The quantity of released oxygen may be quite high as the requirement of charge neutrality is no longer preserved solely by small concentrations of cation vacancies but by the possibly flexible redox behavior of the B site cation(s). However, one requirement for the oxygen vacancies to be mobile is to preserve a cubic perovskite structure [3], where the redox behavior of the B site cation(s) plays the key role as well. Hence, a better understanding of the redox behavior can be used to tailor improved membrane materials with excellent phase stability under strongly reducing conditions.

The pioneering work of Teraoka et al. in the 1980s [4–7] exceeded the already high standards for obtainable oxygen fluxes. As a consequence, the search for high-flux materials (i.e., exhibiting oxygen permeation fluxes of one to two orders of magnitude higher than cubically stabilized zirconia equipped...
with shortcircuit external electrodes [4,8] focused until today mostly on complex perovskites hosting cobalt on their crystallographic B site. The current state-of-the-art material with respect to oxygen permeation and phase stability above 900 °C is (Ba0.5Sr0.5)CoO3−δFe2O3−δ (BSCF) [3,9–11]. Recently, in situ high-temperature electron energy-loss spectroscopy (HT-EELS) on BSCF has shown that cobalt is reduced from an average formal oxidation state of 2.6+ to 2.2+ and iron from 3.0+ to 2.8+, if BSCF is heated in the vacuum chamber of a transmission electron microscope (TEM) from room temperature to 950 °C [12]. The average valence of the B site cations, 2.7+ at room temperature and 2.3+ at 950 °C, give oxygen contents 3 − δ of 2.3 and 2.2, respectively. That is in good agreement with oxygen stoichiometries estimated by thermogravimetric analysis (TGA) and neutron powder diffraction [13]. The experiments in [12] however, give direct proof of the easier reducibility of cobalt over iron in a highly doped perovskite-type oxide. Also, comparative TGA of different perovskite-type materials indicate that during heating the polyvalent B-site cobalt ions are reduced far more easily than iron, manganese or nickel [14].

The flexible redox behavior of cobalt provides on the one hand high oxygen fluxes at high temperatures. On the other hand it leads to two major problems hinder the reliable use of the BSCF material (and cobaltites in general) under important technical requirements. First, it causes a large coefficient of thermal expansion (CTE) that can lie in the range of 20 − 24 × 10⁻⁶ K⁻¹ over a wide temperature range [13,15]. The resulting dilatation causes huge thermal stresses and thus cracks form easily in the membranes, especially if operated at steep oxygen potential gradients. Steep gradients can be obtained by making membranes very thin (i.e., <200 μm) [15–17]. This is of interest to increase flux densities for the design of compact membrane units. Second, the valence instability of cobalt introduces inherent phase instability to the cobaltites at intermediate temperatures (ITs, ca. 500–800 °C) [9,18,19]. This is due to a coupled valence/spin-state transition of cobalt, and cobaltites containing CoO₂⁺ in low-spin configuration tend to prefer face sharing (contributions of hexagonal stacking) rather than corner sharing (cubic stacking) [19]. The breakdown of the cubic perovskite structure principally limits the long-time stability of the BSCF material under the conditions required for the operation of a membrane material in the IT range. The IT range, however, is of special interest for membrane-based dehydrogenation processes in the synthesis of basic chemicals like ethylene [20] and propylene [21] at high selectivity, and for the novel concept of solid oxide fuel cells (SOFCs) [22].

Recently, the search for alternative materials has led to the development of the cobalt-free perovskite-type oxide (Ba₀.₅Sr₀.₅)(Fe₀.₈Zn₀.₂)O₃₋₅ (BSFZ) [23,24]. Wang et al. [24] demonstrated its potential for use in a membrane reactor for the partial oxidation of methane (POM) at 900 °C. The reported oxygen permeation flux of 2.5 ml min⁻¹ cm⁻² on 1.25 mm-thick membranes at 900 °C indicates a high conductivity as well as high surface exchange rates for oxygen. Wei et al. [25,26] quantified the latter by measuring low polarization resistances of 0.22, 0.46, and 0.98 Ω cm⁻² at 700, 650, and 600 °C, respectively. They also used BSFZ as a cathode material in an IT-SOFC at 500–650 °C at power densities up to 180 mW cm⁻². The room temperature structure of BSFZ has been refined in a cubic unit cell (a = 0.3990(0) nm) by the Rietveld method [27]. In situ X-ray diffraction (XRD) has shown that BSFZ remains in the cubic structure if heated to 900 °C in air or in low oxygen partial pressures down to 10⁻¹⁰ Pa [24]. Good phase stability of cubic BSFZ in the IT range has been demonstrated recently for up to 100 h [28] and it is further implied by the observation that the perovskite can be synthesized by a sol-gel-based method in the pure phase at 750 °C [27,29,30]. This is contrary to the cobaltite BSCF that requires higher temperatures in an analogous synthesis (950 °C) [19,31]. The present work focuses on a thorough atomic level understanding of electronic effects in the redox behavior of the BSFZ perovskite. Combined in situ electron energy-loss spectroscopy (EELS) and Mössbauer spectroscopy show that a coupled Fe³⁺/Fe²⁺ valence and Fe³⁺ low-spin to high-spin transition play a key role. This is reflected in anomalies found in integrative investigations of temperature-dependent weight-losses and lattice dilatations.

2. Material and methods

The BSFZ material was synthesized from nitrate precursors via an ethylene-diamine-tetra-acetic acid (EDTA)/citrate acid complexing method at 950 °C for 10 h as described in detail elsewhere [27,29,30]. BSFZ ceramics were sintered at 1150 °C for 10 h and shaped by cutting, grinding, and polishing into disks approximately 3 mm in diameter and 80 μm in thickness. To obtain TEM specimens, these disks were dimple ground from one side to a residual thickness of 10 μm (dimple grinder, model 656, Gatan Inc., Pleasanton, CA, USA). Finally, Ar⁺ ion sputtering was employed at 3 kV under an incident angle of 6° (PIPS, precision ion polishing system, model 691, Gatan Inc.) until electron transparency was achieved.

To obtain a standard for Fe⁰, a metallic iron wire 0.25 mm in diameter (purity 99.99 + %, Chempur) was polished on polymer-embedded diamond foils to a thickness of 50 μm using 1,2-propanediol as a lubricant. The bar was epoxy-glued onto a copper slot grid (1 × 2 mm; 50 μm) and then ion-milled with 3 kV–Ar⁺. The specimen was immediately transferred from the vacuum chamber of the ion mill to the transmission electron microscope (TEM). To prevent the undesired influence of local oxidation of thin specimen areas on the observed EEL fine structures near the L₂,₃ ionization edge of iron (Fe L₂,₃-ELNES), it was carefully checked for the absence of any O-K signal in EEL and energy dispersive X-ray (EDX) spectra. Commercial powders of FeTiO₃ (purity 99.8%, Alfa Aesar, CAS-No. 12022-71-8) and α-Fe₂O₃ (>95%, Riedel-de-Haen, CAS-No. 1309-37-1) were used as standards for Fe²⁺ and Fe³⁺, respectively. FeTiO₃ (ilmene) is a more reliable standard for Fe²⁺ than FeO (wüstite), as the latter is often iron deficient and consists of Fe₁₋ₓO with noticeable contributions of Fe³⁺ [32]. To obtain a standard for Fe⁴⁺, a procedure similar to those chosen in [33,34] was applied: although here an EDTA/citrate acid complexing method (like for the synthesis of the BSFZ material) instead of a solid-state process was used to synthesize SrFeO₃₋₅. Phase purity was confirmed by XRD. Subsequently, stoichiometric SrFeO₃ was observed by filling the lattice with additional oxygen. The additional oxygen was inserted into the lattice using KClO₄ in a gold capsule with an ethylene-diamine-tetra-acetic acid (EDTA)/citrate acid complexing method at 950 °C for 10 h as described in detail elsewhere [27,29,30]. BSFZ ceramics were sintered at 1150 °C for 10 h and shaped by cutting, grinding, and polishing into disks approximately 3 mm in diameter and 80 μm in thickness. To obtain TEM specimens, these disks were dimple ground from one side to a residual thickness of 10 μm (dimple grinder, model 656, Gatan Inc., Pleasanton, CA, USA). Finally, Ar⁺ ion sputtering was employed at 3 kV under an incident angle of 6° (PIPS, precision ion polishing system, model 691, Gatan Inc.) until electron transparency was achieved.

TEM investigations at room temperature (JEM-2100F-CEHR, C₄ = 0.5 mm, C₅ = 1.2 mm, JEOL Ltd., Tokyo, Japan) and at high temperature (CM20 FEG Super TWIN microscope, C₆ = 1.2 mm, C₇ = 1.2 mm, Philips, Eindhoven, Netherlands) were performed at 200 kV with the specimen at 2–4 × 10⁻¹⁰ Pa. Both microscopes were equipped with a post-column imaging filter (GIF, Gatan Inc.) employing a 1024 × 1024 pixel charge-coupled device (CCD) camera and a light-element EDX spectrometer. The Schottky-type emitter gave a full width at half maximum (FWHM) of the zero-loss peak of 1 eV. Calibration of the GIF drift tubes was done using...
the first maximum of the Ni–L$_2$ edge of an NiO standard (853 eV [35]). The energy dispersion of the spectrometer setup at nominally 0.1 eV/pixel was calibrated by acquiring the zero-loss peak with an offset of 50 eV given to the calibrated drift tube and without any offset. All EEL spectra were taken in diffraction-coupled mode. Magnifications of the TEMs were set in combination with a 2 mm entrance aperture of the GIF so that ca. 150 nm circular areas were analyzed. These were carefully chosen to be thin and in the case of powder specimens were not supported locally by a carbon film. An objective aperture was inserted to limit the collection half-angle to ca. 32 mrad, respectively. This means that the dipole selection rule primarily applies and restricts, with respect to parity and angular momentum, the nature of empty states to be probed. In principle this provides measurement of the site, spin-state, and symmetry of the selected ions. To measure the absolute position of core-loss details, pairs of core-loss and low-loss spectra were acquired with 10 s exposure, while the switching of energy ranges was made within a few seconds by removing offsets to the drift tube of the GIF (O-K: 530 eV; Fe–L$_2$3: 710 eV; Ba–M$_{4.5}$: 780 eV). Illumination was almost parallel but was also adjusted for low-loss acquisition by defocusing the condenser lens (CL-3) to avoid overexposure of the CCD camera. The CM200FE was equipped with a double tilting heating holder (model 652-Ta, Gatan Inc.). Heating from room temperature to 900 °C was done with a ramp of ca. 5 °C min$^{-1}$, and the specimen was equilibrated at the respective temperature for 15 min before acquiring in situ EEL spectra.

Scanning electron microscopy (SEM) was made on a field-emission instrument at 2 kV (JSM-6700F, JEOL Ltd., Tokyo, Japan).

Mössbauer spectroscopic measurements were performed in transmission geometry using a conventional spectrometer in constant acceleration mode. In situ spectra were taken in the temperature range of 20–900 °C in air. BSFZ powder specimen was fixed on a quartz support (a 200 μm thick plate). A $^{57}$Co/Rh γ-ray source was used. The velocity scale of the spectra was almost parallel but was adjusted for low-loss acquisition by defocusing the condenser lens (CL-3) to avoid overexposure of the CCD camera. The CM200FE was equipped with a double tilting heating holder (model 652-Ta, Gatan Inc.). Heating from room temperature to 900 °C was done with a ramp of ca. 5 °C min$^{-1}$, and the specimen was equilibrated at the respective temperature for 15 min before acquiring in situ EEL spectra. The Voigt-based fitting method provided distributions of hyperfine parameters for multiple species in a spectrum.

Differential thermoanalysis (DTA) and TGA were measured on 99.5 mg calcined BSFZ powder in a DTA/TG crucible of Al$_2$O$_3$ from 20–1400 °C with a heating rate of 5 °C/min under an air flowrate of 100 ml min$^{-1}$ (STA 429 CD, Netsch, Selb, Germany). The oxygen content of calcined BSFZ powder was measured by the carrier gas hot extraction method with a commercial oxygen analyzer (TC 436DR, Leco, St. Joseph, USA). The powders were weighed (about 20 mg) into a metallic capsule of nickel (0.4 g) with the addition of a tin tablet (0.2 g). This pressed package was dropped into an outgassed high temperature graphite crucible that was electrically heated with a power–time-program. Two infrared selective detectors registered simultaneously the formed reaction species CO and CO$_2$. The calibration was carried out with ZrO$_2$ for the CO detector and with carbon dioxide gas dosing for the CO$_2$ detector. A reproducibility of 0.5% relative standard deviation (RSD) for this method has been shown for many oxides [37].

In situ high-temperature XRD measurements were performed with monochromator-filtered CuKα radiation (Kα$_2$/Kα$_1$: 0.5) at 40 kV and 40 mA with a receiving slit of 0.19 mm (X'pert-MPD instrument, Philips). Data were collected in a step-scan mode in the range of 29–33° 2θ with intervals of 0.02° and count times of 30 s per step. The sample was tested in an HT cell (HDK 2.4 with REP 2000, Edmund Bühler, Hechingen, Germany) with a Pt–Rh holder, which has no reflection in the applied 2θ range. The applied temperature range was 30–1000 °C with 3 C min$^{-1}$ in air and an equilibrium time of 30 min for each data acquisition. The maximum of the (110) reflection was estimated by a combined Gaussian and Lorentzian fitting, and the cell parameters were refined by using TOPAS-Academic V4.1 (Coelho Software, Brisbane, Australia).

Measurements of the linear thermal expansion of BSFZ ceramics were conducted in the 20–1000 °C range, using a difference dilatometer with inductive transducers (DIL 802L, Bähr, Hüllhorst, Germany). Quartz specimens were used for calibration and as inert bodies. To study the influence of $p_{O2}$, the expansion measurements were carried out in a flowing gas atmosphere of argon (0.5 Pa O$_2$) and argon/O$_2$ mixtures under different O$_2$ partial pressures. In all cases, dense rods ($5 \times 2 \times 15$ mm$^3$) with polished frontal faces were successively heated and cooled twice at the rate 5 °C min$^{-1}$. The coefficient of thermal expansion (CTE) follows directly from these measurements as for the cubic perovskite the strain tensor is fully determined by a single scalar [38].

3. Results and discussion

Fig. 1 illustrates the sol–gel-based synthetic process for BSFZ starting from an aqueous solution of stoichiometric amounts of nitrates with EDTA, citric acid, and ammonia. The stage of the gel (after 18 h at 150 °C) is characterized by an ultrafine dispersion of cross-linked metal–organic complexes (bright features in Fig. 1a). The fine-scale intermixing is considered a major advantage over classical solid-state routes if a homogeneous product of complex stoichiometry is desired, as in case of BSFZ. After calcination, the BSFZ perovskite is a fine powder with grains of nanoscale size that are eventually sintered together (Fig. 1b). After green compacting and sintering at ambient pressure, a BSFZ ceramic is obtained with grain sizes in the order of several tens of micrometers (Fig. 1c).

![Fig. 1. From nano to macro. Outline of the sol–gel-based synthetic process with snapshots of different steps: (a) STEM-HAADF of the gel showing finely dispersed and cross-linked metal–organic complexes, (b) SEM of calcined perovskite powder, (c) SEM surface view of grain structure in sintered BSFZ ceramic, (d) photograph of a disk membrane.](image-url)
The grain boundaries in sintered membranes are atomically thin, with the absence of any interfacial phase. A typical example is shown in Fig. 2. The lattice misfit between the (011) lattice planes of grain A (0.282 nm) and the (01 1) lattice planes of grain B (0.178 nm) is accommodated by misfit dislocations (marked by T’s in Fig. 2c). Obviously, it is energetically favorable to reduce strain by leaving every third (01 1) atomic plane of grain B unpaired, and thus loose coherency. In accord with this, it was shown that this kind of grain boundary acts as a barrier for oxygen permeation. In the present article, however, we focus on the bulk properties of the BSFZ material during temperature-induced reduction.

It is therefore essential to have a look at the electronic states or bands in the BSFZ material (Fig. 3). The location of the O:2p states just a few eV below the partly filled Fe:3d states means a small electronic oxygen ligand to iron charge transfer energy \( \Delta_{dp} = \epsilon_{Fe:3d} - \epsilon_{O:2p} \) [42]. This causes partial hybridization in the Fe–O bonds that become strongly polar rather than purely ionic. For the same reason, hybridization of O:2p with unoccupied Zn:4s, Ba:4f, Sr:4d, and Fe:4s is expected (see Fig. 3). Because the occupied O:2p and Zn:3d states are energetically similar, an anomalous valence band cation–anion: p hybridization is expected as well [43].

Starting with an ionic model for iron allows important details of the electronic structure to be derived. The average d electron energy is given by the electrostatic Madelung energy of the ions. Due to intra-atomic exchange coupling, indistinguishable electrons in the partly filled 10 d orbitals cause a splitting by \( \Delta_{fe} \) [44]. This splits the d states for majority spin \( '+' \) and minority spin \( '-' \) (Fig. 4). It has to be taken into account that iron is octahedrally coordinated by oxygen in the cubic perovskite structure. Thus, the additional crystal field splitting \( \Delta \) of the two sets of five d orbitals into three \( t_{2g} \) and two \( e_{g} \) orbitals, respectively, has to be considered. Depending on the relative magnitude of \( \Delta_{ex} \) and \( \Delta \) there are different electronic configurations, three of which are shown in Fig. 4: high-spin Fe\( ^{IV} \) with \( 3d_{5/2}^{0} = (t_{2g}^2)(e_{g}^1)^3 \), low-spin Fe\( ^{III} \) with \( 3d_{5/2}^{3} = (t_{2g}^2)(t_{2g}^2)(e_{g}^1)^2 \), and high-spin Fe\( ^{III} \) with \( 3d_{5/2}^{6} = (t_{2g}^2)(e_{g}^3)^2 \). Consider that the amount of hybridization is different for the three configurations. The \( e_{g} \) orbitals are directed to the ligand, giving a large overlap with 0:2p orbitals. The \( t_{2g} \) orbitals point towards the corners of the cubic unit cell and overlap less with the 0:2p orbitals. It can be assumed that the amount of hybridization of \( e_{g} \) is twice that of \( t_{2g} \) [45] due to a stronger overlap with 0:2p orbitals. As a consequence \( e_{g} \)-derived bands are broader than \( t_{2g} \)-derived bands, even though both bands are narrow.

Fig. 5 shows the room temperature \( L_{2,3} \) energy-loss near-edge structures (ELNESs) of iron in different compounds exhibiting pure valence states [46] compared to the BSFZ material (gray curves).
Because of Fe:2p spin–orbit coupling, the overall spectral shapes are similar for all iron species with an intense peak at around 708–710 eV (\(L_3\)) and a less intense peak at 721–723 eV (\(L_2\)). Respective spectra in Fig. 5 match those obtained for FeO (Fe\(^{2+}\)), LaFeO\(_3\) (Fe\(^{3+}\)), and SrFeO\(_3\) (Fe\(^{4+}\)) by X-ray absorption near-edge structures (XANES) and by multi-electron configuration interaction calculations\(^{[47,48]}\). These findings show that the chemical shift between Fe\(^{0}\), Fe\(^{2+}\), Fe\(^{3+}\), and Fe\(^{4+}\) is in the range of 2 eV, making accurate measurement of the absolute position of fine structure details essential. Positions of the first peak in the \(L_{2,3}\)-ELNES of the Fe\(^{2+}\) and Fe\(^{3+}\) standards still shows some splitting. In contrast, this peak does not show any separation for the Fe\(^{4+}\) standard or BSFZ, and the full width at half maximum is just 3.5 eV and 2.8 eV, respectively. Hence, the energy difference \(|\Delta_{ex} - \Delta_e|\) in BSFZ is even smaller than for all investigated oxide standards. Moreover, it is concluded that the absolute values of \(\Delta_{ex}\) and \(\Delta_e\) are small compared to the actual energy resolution of 1 eV in the experiments. That means that the \(t_{2g}\) and \(e_g\) states are positioned almost at the same energy leading to the competition of high- and low-spin states and the eventual break down of Hund’s rule\(^{[44]}\).

The ELNES of Fe–\(L_{2,3}\) and O-K edges of the BSFZ material were monitored from room temperature to 900 °C. Significant changes in shape or energy position were not observed. Some in situ spectra of Fe–\(L_{2,3}\) are shown in Fig. 6. Over the entire temperature range they show similar features to those discussed for the BSFZ...
spectrum in Fig. 5 with the same peak width and separations, indicating that iron stays in an Fe$^{4+}$/Fe$^{3+}$ mixed valence state during the in situ experiment.

The O K-ELNES of the in situ spectra (Fig. 7) can be divided into three regions: pre-peak A, peak B, and peak C. Pre-peak A (522–530.5 eV) originates from transitions of O:1s electrons into the unoccupied Fe:3d fraction that have 2p character due to hybridization with O:2p orbitals [12,45,52,53]. If compared with [43,54,55], peak B (530.5–546 eV) can be assigned to Zn:4sp, Ba:4f, and Sr:4d orbitals hybridized with O:2p orbitals (see Fig. 3). Neither fitting procedures [12,52] or integration of intensities gave a trend in the relative amount of pre-peak A as a function of temperature. Integration revealed that the relative amount of the pre-peak A intensities in the spectral range from 522–546 eV scatters from 13% to 15%. It is concluded that the amount of O:2p hybridization with Fe:3d relative to that with other metal cations does not change with the bond length expansion associated with lattice dilatation during heating of BSFZ. However, a shoulder in the high-energy flank of peak B is noted at high temperatures, and it remains present after cooling of the specimen to room temperature. It must be noted that if the heating occurs in the vacuum chamber of a TEM, the reverse filling oxygen in the perovskite lattice will not reach the initial level. A more accurate designation of the spectral features in the high-energy flank of peak B would require band structure calculations for this complex perovskite that is beyond the scope of this work. Nevertheless, because the pre-peak A does not show splitting, it is emphasized once again that the energies $\Delta_{ex}$ and $\Delta_{c}$ as well as their difference $|\Delta_{ex} - \Delta_{c}|$ are small in BSFZ under all experimental conditions.

Room temperature Mössbauer spectra of a BSFZ powder before and after heat treatments in air up to 900°C are almost identical (see Fig. 8). However, a small difference is noted that hints to some irreversibility in the oxygen release and pick-up process. The room temperature spectra are well fitted by the superposition of three subspectra (Fig. 8, bottom). Based on their isomer shifts (IS black = 0.19 mm/s, IS light gray = 0.26 mm/s) and on their symmetric quadrupole splitting (QS black = 0.48 mm/s, QS light gray = 1.11 mm/s) these black and light gray subspectra are attributed to Fe$^{IV}$, $(t^2_g)(e^6_g)^1$, and Fe$^{III}$ ions, $(t^5_g)(e^5_g)^2$, respectively, both in octahedral coordination and high-spin configurations [56–58]. The isomer shift of the third subspectrum (IS dark gray = 0.53 mm/s) can be attributed to Fe$^{III}$, $(t^5_g)(e^4_g)$, also in octahedral coordination [56,58–61], but in a low-spin configuration. It should be noted that the dark gray subspectrum shows almost no quadrupole splitting and supports the above made designation of d orbital occupancies that give different electric field gradients at the iron nucleus [58]. The average relative intensities of the subspectra, calculated from the room temperature spectrum before the heating cycle, are as follows: $I_{black} = 67.9\%$, $I_{dark\ gray} = 24.0\%$, $I_{light\ gray} = 8.1\%$. In Fig. 8 it is shown that the dark gray subspectrum disappears with increasing temperature from room temperature to ca. 500°C.

Fig. 7. In situ oxygen K-ELNES of a BSFZ ceramic. Spectra are background subtracted, scaled to the same integral counts in the range of 522–546 eV, and vertically shifted for clarity.

Fig. 8. In situ Mössbauer spectra of BSFZ powder conducted in air. The subspectra are fitted in color (Fe$^{IV}$ black, Fe$^{III}$ dark gray, and Fe$^{III}$ light gray) and are vertically shifted for clarity.
At temperatures above 500 °C, the spectra become narrower. The vanishing of the Fe$^{III}$ fraction from the spectrum indicates a partial spin-state transition by an increase of $\Delta S - \Delta L$ (cf. Fig. 4). The Mössbauer spectra of the sample taken above 500 °C could be fitted by the superposition of just two subspectra (black and light gray). The intensity of the light gray subspectrum increases at the expense of the black one. At 900 °C, the intensities of the light gray and black subspectra are 37.5% Fe$^{III}$ and 62.5% Fe$^{IV}$, respectively (see Table 1 for more details).

If the intensities of the subspectra are taken to indicate the relative amount of different iron species, a very slight reduction of iron is noted; the deduced oxygen stoichiometry $3 - \delta$ of the BSFZ compound does not change significantly, from 2.67 at room temperature to 2.65 at 900 °C, respectively. But the mixed low- and high-spin state of the Fe$^{III}$ ion changes to a purely high-spin configuration. For room temperature the deduced $\delta$ (and corresponding iron valences) are in agreement with Fig. 9, but, at high temperature they deviate remarkably by an underestimation of Fe$^{III}$ by an overestimation of Fe$^{IV}$. The change in iron valencies would be minimal, 3.7+ at room temperature and 3.6+ at 900 °C, respectively. However, the intensities obtained would be minimal, 3.7+ at room temperature and 3.6+ at 900 °C, respectively. But the mixed low- and high-spin state of the Fe$^{III}$ ion changes to a purely high-spin configuration. For room temperature the deduced $\delta$ (and corresponding iron valences) are in agreement with Fig. 9, but, at high temperature they deviate remarkably by an underestimation of Fe$^{III}$.

Remember, the spectral intensities of subspectra are proportional to the recoil-free fraction of various iron species in the sample and can be correlated directly to real concentrations only if constant atomic displacement factors are assumed for all species. Even though in the cubic perovskite the different iron species occupy just one crystallographic site, a measure of likely individual thermal vibration amplitudes has to be estimated by temperature-dependent neutron, X-ray or (convergent beam) electron diffraction on single-crystals combined with appropriate modeling. This is of special concern for the BSFZ perovskite, as the average atomic displacement parameter for the 1b Wyckoff position (iron and zinc) is already high as $B = 2.4 \pm 0.1$ at room temperature [29]. The situation is even more complicated by the complex stoichiometry of BSFZ. However, to allow a reliable quantification of the spectra once additional knowledge about the BSFZ material is obtained, we provide complete spectral information in a condensed form in Table 1.

In addition, it should be mentioned that with increasing temperature there is a large center shift of all subspectra to the left. This means essentially that the charge density at the $^{57}$Fe nucleus decreases [58] even though a contribution from second-order Doppler shift [62,63] should be considered. One principal reason for the observation could be a decrease of the probability density of ligand orbitals (oxygen) at the position of the $^{57}$Fe nucleus when the lattice is thermally dilated. The second principal reason is related to the observed spin-state transition and a change in the population of orbitals with $t_2g$- and $e_g$-character. Remember, the amount of hybridization of $e_g$ orbitals pointing to the ligand, can be assumed to be twice that of $t_{2g}$ orbitals due to larger overlap integrals with O:2p orbitals [45,44].

### Table 1

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<th>$T$ (°C)</th>
<th>Fe$^{III}$ high-spin</th>
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<th>Fe$^{IV}$ high-spin</th>
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<tr>
<td>900</td>
<td>0.46</td>
<td>0.30</td>
<td>62.5</td>
<td>–</td>
</tr>
<tr>
<td>23</td>
<td>0.19</td>
<td>0.51</td>
<td>61.7</td>
<td>+0.53</td>
</tr>
</tbody>
</table>

* A Lorentzian linewidth of 0.24 mm s$^{-1}$ resulting from the fit of the room temperature spectrum of the sample was chosen for the fits of the spectra taken at elevated temperatures. CS refers to the center shift of the whole spectrum.

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**Fig. 9.** DTA and TGA curves of BSFZ with indication of the oxygen content $3 - \delta$. 

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DTA probes the thermal stability of the perovskite by the absence of exo- or endothermic peaks in the temperature range from 100 to 1000 °C (see Fig. 9, right scale). Hence, crystallographic phase transformations or abrupt decomposition can be ruled out. The constant increase of the DTA signal displays an exothermic process spanning from 100 to 900 °C and is attributed to the release of oxygen from the perovskite lattice. The oxygen release is monitored by a continuous weight loss as seen in the TGA curve (Fig. 9, left scale). The slope of the TGA curve becomes distinctly steeper at around 450 °C, correlating with the vanishing of the Feiii fraction (cf. Fig. 8). It should be noted that the resulting high-spin configurations have a higher occupancy of the eg-based states (see Fig. 4) with stronger hybridization effects and thus a higher electronegativity. This is favorable for a larger release rate of oxygen. The accompanied reduction of iron is obviously easier if no spin-flip are involved. However, above 800 °C the mass loss (Fig. 9, left scale) becomes very small and the oxygen release seems to stagnate at a relative weight loss of ca. 1.6 wt%. The DTA shows constant values above 800 °C and decreases above 900 °C, signifying the end of the exothermic process, i.e., the oxygen release. The oxygen content in a BSFZ powder at room temperature was estimated by carrier hot gas extraction to 20.25 ± 0.19 wt% after double heating–cooling in a thermoanalyzer apparatus (STA449, Netzsch, Selb, Germany) between room temperature and 1000 °C at a heating/cooling rate of 20 °C min⁻¹. The measurements gave an oxygen content 3 – δ of about 2.70 ± 0.03. Using this data, the TGA curve can be interpreted directly in terms of the oxygen content in the BSFZ perovskite (Fig. 9, very left scale). It shows a decrease of the oxygen content from 2.70 at room temperature to 2.50 at 900 °C. That corresponds to a reduction of iron from an average valence of 3.75+ down to 3.25+, if the other cations are considered to have a constant valence: Ba²⁺, Sr²⁺, and Zn²⁺. In other words, iron in BSFZ is in a mixed 75% Fe⁴⁺/25% Fe³⁺ valence at room temperature. Upon heating to 900 °C in air it will be reduced to a 25% Fe⁴⁺/75% Fe³⁺ valence. We should mention that the TGA curve in Fig. 9 agrees with the one published by Wei et al. [26] for the heating of BSFZ in air. However, their room temperature value for the oxygen content estimated by iodometric titration is lower (2.59). Thus, they implicitly predict a reduction of iron to less than 3+ with some Fe⁵⁺ species being present. However, this can be ruled out by Mössbauer spectroscopy (Fig. 8) as well as by EELS (Figs. 5 and 6). We state that our results are self-consistent.

In situ XRD patterns of a BSFZ powder in air and in reducing gas mixtures (Ar, 2% O₂–Ar, and 2% H₂–Ar) in the 2θ range of 20°–90° from room temperature to 900 °C have been presented in [24]. They show excellent phase stability under all applied conditions by the conservation of the cubic perovskite structure. Fig. 10 shows the 2θ angular position of the (110) reflection of the cubic BSFZ during in situ heating in air up to 1000 °C with indication of the respective lattice parameters. The absolute peak position after the heating cycle is shifted by 0.1° towards larger angles and indicates that the changes are not completely reversible, probably due to kinetic effects. This is consistent with observations by EELS (cf. Fig. 7) and Mössbauer spectroscopy (cf. Fig. 8). A change in the rate of expansion of the BSFZ powder crystals is noted between 400 and 600 °C. From these XRD data, the CTE is estimated to be around 11 × 10⁻⁶ and 24 × 10⁻⁶ K⁻¹ in the temperature ranges 30°–400 °C and 600–1000 °C, respectively.

The dilatometric measurement of the CTE for a BSFZ ceramic is presented in Fig. 11 as a function of different oxygen partial pressure. The measurements were conducted at 11 × 10⁻⁶ and 20 × 10⁻⁶ Pa, and under Ar. The CTE is nearly independent of the oxygen partial pressure pO₂, although it slightly decreases with decreasing pO₂. There is a constant CTE between 300–600 °C of ca. 15 × 10⁻⁶ K⁻¹ and between 750 and 1000 °C of ca. 22 × 10⁻⁶ K⁻¹, which corresponds to the XRD data obtained on powders. Strain-induced phase transitions can be ruled out by the in situ XRD and DTA observations. Therefore, the CTE in the current experiment is a combination of a steady thermal expansion caused by anharmonic thermal lattice vibrations and an additional term of a chemical expansion [64,65] due to the coupled valence/spin-state transition of iron and the accompanied increase of its ionic radius during heating.
4. Conclusions

The performed EELS, esp. ELNES analyses of the Fe–L2,3 edge have revealed that iron in the BSFZ perovskite is in a mixed Fe4+/Fe3+ valence state at room temperature. Upon heating to 900 °C the reduction of iron is so weak that no Fe2+ species are involved. Moreover, at the O-K edge hybridization effects of O:2p orbitals with empty Fe:3d, Zn:4s, Ba:4f, Sr:4d, and Fe:4s orbitals are noticed. The relative amount of hybridization does not change upon heating of the BSFZ perovskite. Mössbauer spectroscopy identified a gradual spin-state transition of the Fe3+ species from a mixed low-spin/high-spin configuration to a high-spin configuration. Above ca. 500 °C the Fe3+ fraction is in a pure high-spin state. The Fe4+ fraction is in a pure high-spin state under all applied conditions. Concerning the redox state of iron, weights of Mössbauer subspectra give a reliable estimate at room temperature only. At elevated temperatures obviously the Fe3+ recoil-free fraction is lower than the Fe4+ recoil-free fraction as a consequence of different temperature coefficients of the respective atomic displacement parameters. However, the accurate determination of the oxygen content by carrier hot gas extraction (3 − δ = 2.70) gave an average Fe valence of 3.75+ in BSFZ at room temperature. Based on these values, monitoring the released amount of oxygen by weight loss upon heating shows that the oxygen content drops to 2.50 and iron is reduced to an average valence of 3.25+ at 900 °C in air. The oxygen release rate and the accompanied reduction of iron increase at around 450 °C, which is the Fe4+ spin-state transition. The spin-state transition also reflects in an increase of lattice expansion above ca. 600 °C as monitored by XRD and dilatometry. Consider that unusual thermal expansion has been reported also in the spin-state transition of LaCoO3 [66]. Note that for BSFZ the quadrupole splitting of Fe4+ and the isomer shifts show discontinuities at the spin-state transition (see Table 1). Similar observations have been made in case of a pressure-induced spin-state transition of LaFeO3 [67].

The spin-state transition should be elucidated in more detail. Since the intra-atomic exchange coupling $J_{\text{ex}}$ decreases with larger radial extension of the crystalline wave functions [44], $J_{\text{ex}}$(Fe4+) exceeds $J_{\text{ex}}$(Fe3+). Increasing $J_{\text{ex}}$ with decreasing hybridization is forced by a lattice expansion in our experiments. Contrary, the cubic ligand field splitting $A_{0}$ increases with increasing hybridization and $A_{0}$(Fe4+) > $A_{0}$(Fe3+). An increase of the Fe–O distance, and thus smaller Fe4+ hybridization is forced by a lattice expansion in our experiments. The cubic ligand field splitting $A_{0}$ increases with decreasing hybridization and $A_{0}$(Fe4+) > $A_{0}$(Fe3+). An increase of the Fe–O distance, and thus smaller Fe4+ hybridization is forced by a lattice expansion in our experiments. The cubic ligand field splitting $A_{0}$ increases with decreasing hybridization and $A_{0}$(Fe4+) > $A_{0}$(Fe3+). An increase of the Fe–O distance, and thus smaller Fe4+ hybridization is forced by a lattice expansion in our experiments. The cubic ligand field splitting $A_{0}$ increases with decreasing hybridization and $A_{0}$(Fe4+) > $A_{0}$(Fe3+). An increase of the Fe–O distance, and thus smaller Fe4+ hybridization is forced by a lattice expansion in our experiments. The cubic ligand field splitting $A_{0}$ increases with decreasing hybridization and $A_{0}$(Fe4+) > $A_{0}$(Fe3+). An increase of the Fe–O distance, and thus smaller Fe4+ hybridization is forced by a lattice expansion in our experiments. The cubic ligand field splitting $A_{0}$ increases with decreasing hybridization and $A_{0}$(Fe4+) > $A_{0}$(Fe3+) and removal of oxygen from the lattice to a reduction. For the heating of BSFZ, reduction of iron from Fe4+ to Fe3+ is compensated partly by the O:2p band. Lowering $p_{o}$ in the surrounding atmosphere, i.e., picking more oxygen from the perovskite lattice, gives two electrons per removed oxygen atom to the lattice and may enhance hybridization of Fe3d−O:2p bonds. The Fe–O bonds become stronger with decreasing $p_{o}$ and we expect a smaller CTE. This systematic trend can be seen in Fig. 11.

We restricted our discussion of the electronic structure in context with Fig. 3 somehow to a simple ionic model with electrons being localized around iron sites to highlight some important points. However, the excellent transport properties of BSFZ for oxygen ions and electrons [24–26] suggest further investigations of the $t_{2g}$- and $e_{g}$-based energy bands are warranted. The $e_{g}$ orbitals with higher amount of hybridization give broader bands. The partly filled $t_{2g}$- and $e_{g}$-based bands are narrow and not widely separated, which is essential in the observed spin-state transition and indicated by the sharp first peak (2.8 eV FWHM) in the Fe L2,3-ELNES (Figs. 5 and 6). The spin-state transition is manifested in the crossing and finally the separation of $t_{2g}$- and $e_{g}$-based bands. A maximum in the electrical conductivity of BSFZ at around 600 °C (9.4 S cm$^{-1}$) observed by Wei et al. [26], manifests a transition from thermally activated polaronic electron hopping to metallic conduction, which was pointed out by some authors to be equivalent with a spin-state transition [70,71]. Comparison with structural field maps [72–74] indeed shows that BSFZ is located close to the borderline of localized to itinerant behavior of the iron d electrons, which can be crossed by changes in stoichiometry or external parameters, and unusual properties can be expected.

Oxygen K-ELNES showed that the amount of O:2p hybridization with Fe:3d relative to other metal cations (Zn:4s, Ba:4f, and Sr:4d) does not change with the bond length expansion associated with lattice dilatation during heating of BSFZ. This is in clear contrast to observations in the BSCF perovskite, which show a relative shift in hybridization of O:2p with Ba:4f and Sr:4d upon Fe:3d and Co:3d [12]. The comparison with [43] makes the relative stabilization of transition-metal–oxygen-ligand to earth alkaline-metal–oxygen-ligand hybridization plausible by an anomalous Zn:3d–O:2p hybridization caused by a very small energy difference (cf. Fig. 3).

It is worth noting that the lowest temperature of successful synthesis of BSCF (950 °C) [19,31] or BSFZ (750 °C) [27,29,30] correlates with spin-state transitions of one of the polyvalent transition metal ions. As already mentioned, it has to be emphasized that both, valence and spin-state, modify the effective radii of transition metal cations, which govern Goldschmidt’s tolerance factor, providing a principal criterion for the expectable perovskite symmetry. Therefore, a careful choice of a membrane material for specific operational conditions has to take into account, that a high stability of the cubic perovskite structure can only be achieved in a pure high-spin state material with its higher ionic radius. This is seen as a big advantage for BSFZ in the IT...
range compared to BSF. However, spin-state transition and its effect on the functionality of membrane materials must be investigated in more detail.

Integration over the CTE from room temperature to 700°C (Fig. 11) gives a dilatation of 0.94% for BSFZ, compared to 1.6% for the cobaltite BSF (based on the CTE given in [11]). The relatively low dilatation of the BSFZ material combined with the peculiar redox behavior of iron, good transport properties, and phase stability [24–26] makes it superior to cobalites for prospective applications in the intermediate temperature range (500–800°C).

5. Summary

It has been shown that the iron in the BSFZ perovskite has a mixed 75% Fe4+ /25% Fe3+ valence (3.75+) at room temperature. Upon heating to 900°C in air it is reduced to a 25% Fe4+ /75% Fe3+ valence (3.25+). The Fe4+ fraction is always in a high-spin state, and the Fe3+ fraction makes a transition from a predominantly low-spin to a pure high-spin configuration at intermediate temperatures. A decrease in the amount of Fe3d–O2p hybridization during lattice expansion is seen as the reason for the spin-state transition as the exchange coupling \( J_x \) increases and the cubic ligand-field splitting \( A_e \) decreases for each species. The coupled valence/spin-state transition is seen as anomalies of weight-loss, due to release of oxygen, and thermal expansion behavior. It is concluded that to provide excellent phase stability and the Fe3+2 /Fe3+1:2 oxidation states of Mn and Fe in various compound oxidants, upon heating to 900°C, the cubic ligand-field splitting \( A_e \) decreases for each species. The coupled valence/spin-state transition is seen as anomalies of weight-loss, due to release of oxygen, and thermal expansion behavior. It is concluded that to provide excellent phase stability and the Fe3+2 /Fe3+1:2 oxidation states of Mn and Fe in various compound oxidants, upon heating to 900°C, the cubic ligand-field splitting \( A_e \) decreases for each species.
The RT Fe...