Mixed Conductivity and Stability of CaFe$_2$O$_4$–δ

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The total conductivity of CaFe$_2$O$_4$–δ, studied in the oxygen partial pressure range from 10$^{-17}$ to 0.5 atm at 1023–1223 K, is predominantly p-type electronic under oxidizing conditions. The oxygen ion transfer numbers determined by the steady-state oxygen permeation and faradaic efficiency measurements vary in the range of 0.2 to 7.2 × 10$^{-4}$ at 1123–1273 K, increasing with temperature. No evidence of any significant cationic contribution to the conductivity was found. The Mössbauer spectroscopy, thermogravimetry, and X-ray diffraction (XRD) showed that the orthorhombic lattice of calcium ferrite is essentially intolerant to the oxygen vacancy formation and to doping with lower-valence cations, such as Co and Ni. The oxygen nonstoichiometry (δ) is almost negligible, 0.0046–0.0059 at 973–1223 K and p(O$_2$) = 10$^{-5}$–0.21 atm, providing a substantial dimensional stability of CaFe$_2$O$_4$–δ ceramics. The average linear thermal expansion coefficients, calculated from the controlled-atmosphere dilatometry and high-temperature XRD data, are (9.6–13.9) × 10$^{-6}$ K$^{-1}$ in the oxygen pressure range from 10$^{-6}$ to 0.21 atm at 873–1373 K. Decreasing p(O$_2$) results in a modest lattice contraction and in the p–n transition indicated by the conductivity and Seebeck coefficient variations. The phase decomposition of CaFe$_2$O$_4$–δ occurs at oxygen chemical potentials between the low-p(O$_2$) stability limit of Ca$_3$Fe$_5$O$_{12–δ}$ brownmillerite and the hematite/magnetite boundary in binary Fe–O system.

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Oxide materials with mixed oxygen-ionic and electronic conductivity attract significant attention for high-temperature electrochemical applications, in particular, electrodes of solid oxide fuel cells (SOFCs) and dense ceramic membranes for oxygen separation and partial oxidation of light hydrocarbons.1–5 The general requirements associated with these applications include a high oxygen permeability, thermodynamic stability in a wide range of temperature and oxygen partial pressure, moderate thermal and chemical expansion, and low reactivity with CO$_2$ and water vapor that may be present in air or in hydrocarbon conversion products. A promising combination of the transport properties and stability is known for perovskite-related ferrites derived from CaFe$_2$O$_4$.4,5 Nonetheless, brownmillerite-like polymorphs.4,11 However, these materials may suffer from hydration and high-temperature XRD data, are

Another phase in the ternary Ca–Fe–O system, stable in a wide temperature range, is CaFe$_2$O$_4$.12 The orthorhombic crystal structure of this compound (space group Pbnm, no. 62) has two distinct iron sites; Ca$^{2+}$ cations occupy pseudotriangular tunnels formed by the corner- and edge-shared FeO$_6$ octahedra.13,16 In air, the total electrical conductivity of CaFe$_2$O$_4$ is predominantly electronic, at least above 723 K.15,17 The ionic contribution to the conductivity at elevated temperatures is mainly provided by O$^{2-}$ anion migration.17 The atomistic computer simulations17 showed that the Ca$^{2+}$ cation transport might also be possible, but is hampered due to energetic factors, namely, unfavorable vacancy formation in the calcium sites. In fact, a significant cationic conduction was only achieved when calcium is replaced by small Li$^+$ cations, charge-compensated by Sn$^{4+}$ doping in the ion sublattice.16,18 Information available on the defect formation and electronic transport processes in CaFe$_2$O$_4$ is still scarce.

This work was centered on the analysis of the oxygen partial pressure dependencies of total conductivity, ion transference numbers, and Seebeck coefficient of CaFe$_2$O$_4$. Particular emphasis was also focused on the chemical expansion induced by minor oxygen-nonstoichiometry variations and on stability of CaFe$_2$O$_4$ at reduced oxygen pressures. In addition, phase equilibria in (Ca,Sr)(Fe,M)$_2$O$_{18−δ}$ (M = Cr, Mn, Ni, Co) systems were assessed in order to evaluate the solubility of dopants, which might be used to alter defect concentrations and transport properties of CaFe$_2$O$_4$.

Experimental

Submicrometer powder of CaFe$_2$O$_4$ was prepared by glycine-nitrate process (GNP)19 using Ca(NO$_3$)$_2$·4H$_2$O and Fe(NO$_3$)$_3$·9H$_2$O as starting materials. The molar glycine/nitrate ratio was double the stoichiometric value calculated, assuming that N$_2$, CO$_2$, and H$_2$O are the only gaseous reaction products. After synthesis, the powder was annealed at 1173 K for 2 h to remove organic residuals and pressed at 150–200 MPa. Gas-tight ceramic samples with relative density higher than 95% were sintered in air at 1423 K for 15 h and then slowly cooled (1–2 K/min) to achieve equilibrium oxygen content at low temperatures. The overall cation composition was confirmed by the inductively coupled plasma (ICP) spectroscopic analysis, which showed that the deviation from nominal Ca/Fe cation ratio is within the limits of experimental error (difference 0.1 atom %); the same conclusion was drawn earlier on the basis of Rietveld refinement results.1 The powdered samples necessary for X-ray diffraction (XRD), Mössbauer spectroscopy, and thermogravimetric analysis (TGA) were obtained by grinding sintered ceramics. Additional series of ceramic samples used for the analysis of phase composition and iron states at elevated temperatures were annealed in various atmospheres for 20–25 h and then quenched.

The procedure to prepare Ca$_{0.5}$Sr$_{0.5}$Fe$_2$O$_4$ and CaFe$_1$M$_{0.5}$O$_4$ (M = Cr, Mn, Ni, Co) was similar to that for undoped calcium ferrite. These powders were additionally annealed in air at
1273–1463 K for 50 h with multiple intermediate grindings and XRD inspections; ceramic samples were sintered at 1423–1593 K.

Detailed descriptions of experimental techniques and equipment used for materials characterization can be found elsewhere.6,7,11,12,20–23 The room-temperature XRD patterns were collected using a Rigaku D/Max-B diffractometer (Cu Kα) radiation, 2θ = 10–100°, step 0.02°. The high-temperature XRD studies were conducted on a Philips X’Pert Pro instrument (2θ = 5–80°, step 0.015°, Anton Paar HTK-2000 heating stage) at 298–1373 K in air or under vacuum (total pressure of 5 × 10⁻⁵ to 5 × 10⁻⁷ atm); the equilibration time was 1–4 h. Rietveld analysis of the diffraction data was performed using the GSAS suite with EXPGUI front-end24,25 and Fullprof software.26 The microstructural studies were carried out using a Hitachi S-4100 scanning electron microscope (SEM) equipped with a Rontec ultra high vacuum detection system for energy-dispersive spectroscopy (EDS). The Mössbauer spectra were obtained at 295 K in transmission mode using a conventional constant-acceleration spectrometer and a 25 mCi ⁵⁷Co source in Rh matrix; the velocity scale was calibrated using α-Fe foil. The spectra were fitted to lorentzian lines using a nonlinear least-squares method,27 constraining the relative areas and line-widths of both peaks in each quadrupole doublet to remain equal.

The total oxygen content was determined by TGA (Setaram SetSys 16/18 instrument); the measurements were carried out in flowing dry air and Ar at 973–1223 K (50 K steps with 2–20 h dwells), followed by complete reduction into calcium oxide and metallic iron in a flow of dried 10% H₂–90% N₂ gas mixture at 1373–1423 K for 35 h. A vertical Linseis L75V/1250 dilatometer was used to study thermal and chemical expansion. The dilatometric measurements were performed at 923–1223 K in air and in a flowing Ar–O₂ gas mixture where the oxygen partial pressure, p(O₂), was fixed at 6 × 10⁻⁴ atm; the temperature steps and equilibration time at each temperature were 50 K and 2–7 h, respectively. The total conductivity (four-probe dc) and Seebeck coefficient were measured in the oxygen partial pressure range from 0.4 down to 8 × 10⁻¹⁵ atm at 650–1280 K, as described elsewhere.20 The oxygen ionic transport was studied at 1123–1273 K by the steady-state oxygen permeability (OP) and faradic efficiency (FE) techniques.21-23 For all OP and FE data presented in this work, the oxygen partial pressure (p₂) at the membrane feed side (OP) or cathode (FE) corresponds to 0.21 atm. In the case of FE measurements under nonzero oxygen pressure gradients, the results were corrected for steady-state oxygen permeation fluxes; for each p(O₂) gradient, the permeation flux was determined independently prior to the FE tests.21-23

Results and Discussion

Structural and microstructural characterizations.—XRD analysis showed that both GNP-synthesized powder and sintered ceramics of CaFe₂O₄ are single-phase (Fig. 1a). The crystal structure was identified as orthorhombic (space group Pbmm); the unit cell parameters (Table I) correspond well to the literature data.14,15,18 Table I lists selected bond lengths calculated from the XRD data. One typical SEM image showing the microstructure of dense CaFe₂O₄ ceramics is presented in Fig. 2. The average grain size was 5–12 μm; no compositional inhomogeneities were detected by the EDS analysis within the limits of experimental uncertainty.

The high-temperature XRD studies demonstrated that CaFe₂O₄ phase is stable in the approximate temperature ranges of 300–1400 K in air and 300–1000 K at p(O₂) = 10⁻⁵–10⁻³ atm under vacuum (Fig. 3). Heating up to 1370 K in vacuum leads to decomposition into a mixture of Ca₂Fe₂O₆, brownmillerite and Fe₂O₃. The limited phase stability of CaFe₂O₄ in moderately reducing atmospheres was further confirmed by the data on total conductivity and thermopower vs oxygen partial pressure, discussed below.

Figure 1b presents the room-temperature XRD patterns of Ca₀.₅Sr₀.₅Fe₂O₄ and CaFe₂₋ₓM₀ₓO₄ (M = Cr, Mn, Ni, Co), all equilibrated in air. The substitution of chromium for iron in CaFe₁₋ₓCrₓO₄ leads to solid solution formation, at least up to x = 0.5. Brownmillerite-type Ca₃(Fe,M₁)O₆ and Fe₂O₃ phases were observed to segregate on doping with 25 mol % cobalt or nickel. In the XRD pattern of CaFe₁₋ₓMnₓO₄, the reflections of CaFe₂O₄ phase coexist with very small impurity peaks, in agreement with data on a relatively narrow compositional range, where Ca(Fe,Mn)₂O₃ solid solution is formed. In the case of Ca₀.₅Sr₀.₅Fe₂O₄, the substitution of Ca²⁺ by larger Sr²⁺ cations causes complete decomposition into the brownmillerite- and Fe₂O₃-based phases. These results show that the number of dopants, which could be used to modify ionic and electronic transport in Fe₂O₃, is very limited. In fact, only the solubility of chromium seems sufficient for this purpose. However, the oxygen ionic conduction in Fe₂O₃ occurs at least to a significant extent, via the vacancy migration mechanism;¹¹ chromium cations are expected to exhibit a donorlike behavior and, thus, to decrease the oxygen vacancy concentration. Consequently, major attention in this work was focused on undoped CaFe₂O₄ ceramics; selected properties of Fe₂O₃ were measured for the sake of comparison. Note that the low solubility of acceptor-type dopants, such as Ni²⁺/³⁺, suggests that the orthorhombic lattice of CaFe₂O₄ is almost intolerant to the oxygen vacancy formation.
Oxygen stoichiometry, Mössbauer spectra, and chemical expansion.—The thermogravimetric studies revealed that in oxidizing atmospheres, \( \text{CaFe}_2\text{O}_4^{\delta-} \) is almost oxygen stoichiometric, although a tendency to minor anion deficiency can be revealed. At \( 973–1223 \text{ K} \), the values of nonstoichiometry \( \delta \) vary in the narrow ranges 0.0046–0.0048 in flowing dry air and 0.0056–0.0059 in argon, increasing on heating. These deviations from stoichiometry are larger than the reproducibility error, but the overall level of oxygen deficiency is very low, comparable to other possible experimental uncertainties. Such uncertainties might result, for example, from minor compositional inhomogeneities at the grain boundaries. At the same time, no essential deviations from the nominal cation composition were detected by the ICP and energy-dispersive spectroscopic analyses; moreover, these uncertainties cannot lead to the systematic variations of oxygen nonstoichiometry with the oxygen partial pressure, observed experimentally. Whatever the mechanism, the corresponding deviations of the average oxidation state of iron cations from 3+ are lower than the Mössbauer spectroscopy detection limits. Respectively, the room-temperature Mössbauer spectra of \( \text{CaFe}_2\text{O}_4^{\delta-} \) equilibrated under oxidizing or moderately reducing conditions consist of only two quadrupole doublets; for both signals, the isomer shift \( \text{IS} \) values are typical of octahedrally coordinated \( \text{Fe}^{3+} \) in the high-spin state \( ^2\text{Eg} \), and the quadrupole splittings are similar to those reported in literature \( \text{Fig. 4 and Table II} \). Neither \( \text{Fe}^{4+} \) nor \( \text{Fe}^{2+} \) cations can be detected, thus confirming that the oxygen deficiency is \(<0.5\% \) in all cases. The estimated relative areas of the doublets, which relate to the two different crystallographic positions of iron in \( \text{CaFe}_2\text{O}_4^{\delta-} \) structure, are almost equal to each other.

### Table I. Selected interatomic distances in \( \text{CaFe}_2\text{O}_4 \) lattice at room temperature.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length, Å</th>
<th>Bond</th>
<th>Length, Å</th>
<th>Bond</th>
<th>Length, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Ca-O}_2 \times 2 )</td>
<td>2.323(4)</td>
<td>( \text{Fe}_1-\text{O}_3 )</td>
<td>2.031(6)</td>
<td>( \text{Fe}_2-\text{O}_3 \times 2 )</td>
<td>1.983(4)</td>
</tr>
<tr>
<td>( \text{Ca-O}_4 \times 2 )</td>
<td>2.333(4)</td>
<td>( \text{Fe}_1-\text{O}_4 )</td>
<td>2.045(5)</td>
<td>( \text{Fe}_2-\text{O}_2 \times 2 )</td>
<td>2.090(4)</td>
</tr>
<tr>
<td>( \text{Ca-O}_1 \times 2 )</td>
<td>2.480(4)</td>
<td>( \text{Fe}_1-\text{O}_1 \times 2 )</td>
<td>2.052(3)</td>
<td>( \text{Fe}_2-\text{O}_1 )</td>
<td>2.066(5)</td>
</tr>
<tr>
<td>( \text{Ca-O}_3 )</td>
<td>2.540(6)</td>
<td>( \text{Fe}_1-\text{O}_1 \times 2 )</td>
<td>2.098(3)</td>
<td>( \text{Fe}_2-\text{O}_1 )</td>
<td>2.120(5)</td>
</tr>
<tr>
<td>( \text{Ca-O}_3 )</td>
<td>2.564(6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The unit cell parameters are \( a = 10.6969(2) \) Å, \( b = 9.2257(2) \) Å, and \( c = 3.0197(1) \) Å; space group \( \text{Pbnm (no. 62)} \); the agreement factors of structure refinement were \( R_p = 5.00\% \), \( R_{wp} = 6.68\% \), and \( \chi^2 = 3.01 \).

**Figure 2.** SEM images of polished and thermally etched \( \text{CaFe}_2\text{O}_4 \) ceramics.

**Figure 3.** High-temperature XRD patterns of \( \text{CaFe}_2\text{O}_4^{\delta-} \) in air and in vacuum.

**Figure 4.** Room-temperature Mössbauer spectra of \( \text{CaFe}_2\text{O}_4^{\delta-} \) equilibrated at various oxygen partial pressures. The calculated functions plotted on the experimental data points are the sums of two quadrupole doublets (Table II), shown slightly shifted for clarity.
for the samples equilibrated at low temperatures in air and annealed at 1223 K and \( p(O_2) = 10^{-5} \) atm (Table II). Further reduction of the oxygen partial pressure down to \( 10^{-10} \) atm leads apparently to changing the iron site concentration ratio, probably due to local distortions and partial reorientation of FeO\(_6\) polyhedra induced by oxygen losses. Similar behavior was observed earlier for acceptor-doped ferrite garnets, where the lattice packing is also not closest.\(^{29}\) Note that \( \text{CaFe}_2\text{O}_4\) remains single phase under these conditions.

The local structural changes near oxygen vacancies, in particular, tilting of the iron-oxygen octahedra, may also be responsible for the lattice contraction on reduction, which was revealed by both dilatometry (Fig. 5a) and high-temperature XRD (Fig. 6). One should mention that the average TECs calculated from the dilatometric and XRD data are in a good agreement, demonstrating reliability of the results. The TEC values determined by these two techniques at 873–1373 K in air are both equal to \( 13.9 \times 10^{-6} \text{ K}^{-1} \) (Table III). The lattice expansion on heating has an anisotropic character (Fig. 6), as for \( \text{CaFe}_2\text{O}_4\) brownmillerite.\(^{12}\) Because of the chemically induced lattice contraction on reduction, the average TECs decrease moderately with decreasing oxygen pressure. The incorporation of chromium cations in \( \text{CaFe}_2\text{Cr}_x\text{O}_4\) lowers the TECs (Fig. 5a and Table III) but raises chemical contraction (Fig. 5b). Regardless of these small changes, both \( \text{CaFe}_2\text{O}_4\) and \( \text{CaFe}_2\text{Cr}_x\text{O}_4\) ceramics appear to possess a relatively high dimensional stability on cycling the oxygen partial pressure and temperature as a result of low variations of the oxygen stoichiometry; their chemical expansivity is comparable to that of perovskite-type chromites\(^{31}\) and layered nickelates.\(^{32}\)

**Electronic and ionic conduction.**—The total conductivity (\( \sigma \)) of \( \text{CaFe}_2\text{O}_4\) is lower than that of \( \text{Ca}_3\text{Fe}_2\text{O}_5\) brownmillerite\(^{12}\) (Fig. 7) but exhibits a similar activation energy (\( E_a \)), suggesting that electronic transport mechanisms in these phases are similar. Decreasing temperature leads to a progressive decrease of \( E_a \) values from 50 to 23 kJ/mol (Table IV), in correlation with the oxygen nonstoichiometry changes. The latter tendency seems to support the above hypothesis on significant lattice distortions near oxygen vacancies.

Doping with chromium has a rather negligible effect on the conductivity at 870–1300 K and increases electronic transport in the low-temperature range.

The results on oxygen ionic conductivity (\( \sigma_{O^2} \)) calculated from the oxygen permeability and faradic efficiency data (Fig. 8), confirm that the total conductivity of \( \text{CaFe}_2\text{O}_4\) is predominantly electronic. The oxygen ion transference numbers vary in the range (0.2–7.2) \( \times 10^{-4} \) at 1123–1273 K in air, increasing with temperature. Furthermore, as discussed below, the time-independent oxygen fluxes under either applied voltage (FE) or oxygen chemical potential gradients (OP) and the results of subsequent EDS analysis all show that cationic conduction, if any, is much lower than oxygen anionic. This makes it possible to neglect the ionic contribution in the analysis of total conductivity and Seebeck coefficient (\( \alpha \)) as a function of the oxygen partial pressure.

Figure 9 shows the variations of electrical properties of \( \text{CaFe}_2\text{O}_4\) in the \( p(O_2) \) range, where no phase transformations were detected by XRD. In oxidizing atmospheres, the total conductivity and thermopower both decrease on reducing \( p(O_2) \) under oxidizing conditions, whereas the Seebeck coefficient has a positive sign, unambiguously indicating the dominant role of the p-type electronic transport. At moderately lower oxygen pressures, a plateau-like behavior is observed. Further reduction leads to a conductivity minimum indicative of the p-n transition, which corresponds to approximately zero values of the Seebeck coefficient as marked by the dashed line in Fig. 9 for the isotherms at 1023 K. Beyond the minimum at still lower \( p(O_2) \), the conductivity starts to increase due to the increasing contribution of n-type electronic transport; the Seebeck coefficient becomes negative.

Taking into account that the TGA and Mössbauer spectroscopy confirmed a predominantly trivalent state of iron cations in \( \text{CaFe}_2\text{O}_4\), these trends may only be explained in terms of the electronic charge-carrier generation due to intrinsic disordering as a main factor governing the conductivity variations; the concentrations of mobile electrons and holes should be small compared to the corresponding densities of states. Another important conclusion refers to a relatively low mobility of the n-type charge carriers. The latter is directly evidenced by the fact that, in oxidizing and moderately reducing atmospheres when the hole concentration in oxygen-deficient \( \text{CaFe}_2\text{O}_4\), should be lower than that of electrons according to the crystal electroneutrality condition, the p-type electronic conduction prevails. This phenomenon may originate from the strong energetic affinity of \( \text{Fe}^{3+} \) cations in \( \text{CaFe}_2\text{O}_4 \) to form binary

### Table II. Parameters estimated from the room-temperature Mössbauer spectra of \( \text{CaFe}_2\text{O}_4\)

<table>
<thead>
<tr>
<th>Equilibration conditions</th>
<th>IS (mm/s)</th>
<th>QS (mm/s)</th>
<th>( \Gamma ) (mm/s)</th>
<th>I (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slowly cooled down to 295 K in air</td>
<td>0.37</td>
<td>0.30</td>
<td>0.32</td>
<td>49</td>
</tr>
<tr>
<td>Annealed at 1223 K and ( p(O_2) = 10^{-5} ) atm</td>
<td>0.37</td>
<td>0.75</td>
<td>0.32</td>
<td>51</td>
</tr>
<tr>
<td>Annealed at 1173 K and ( p(O_2) = 10^{-10} ) atm</td>
<td>0.37</td>
<td>0.29</td>
<td>0.31</td>
<td>49</td>
</tr>
</tbody>
</table>

Notes: IS, QS, \( \Gamma \), and I are the isomer shift relative to metallic \( \alpha \text{-Fe} \) at 295 K, quadrupole splitting, full width at half maximum, and relative area, respectively. Estimated standard deviations are <1% for I and <0.02 mm/s for the other parameters.
and ternary clusters with oxygen vacancies as revealed by the computer simulations; consequently, most of the n-type electronic charge carriers should be trapped. Whatever the trapping mechanisms, analogous behavior is well known for a variety of Fe-containing oxide phases with perovskite- and apatite-like structures (e.g., Ref. 33-35, and references cited). Neglecting any site-exclusion effects and transported heat of the electronic carriers, the electrical conductivity, and Seebeck coefficient may be described as

$$\sigma = \left( \mu_\text{p} \cdot p + \mu_\text{n} \cdot n \right) \cdot e \cdot N_{\text{uf}}/V_{\text{uc}} \quad [1]$$

$$\alpha = \frac{k}{e} \ln \left( \frac{2}{p} \right) - \left( 1 - \frac{k}{e} \right) \ln \left( \frac{2}{n} \right) \quad [2]$$

where \( t_\text{p} \) is the hole transference number, \( n \) and \( p \) are the concentrations of electrons and holes per unit formula, \( \mu_\text{n} \) and \( \mu_\text{p} \) are their mobilities, \( N_{\text{uf}} = 4 \) is the number of formula units per unit cell, and \( V_{\text{uc}} \) is the unit-cell volume calculated from the XRD data. In these equations, all iron cations are assumed energetically equivalent because the Fe–O bond lengths for different crystallographic sites are quite similar (Table I). At the oxygen partial pressures close to atmospheric, high values of the Seebeck coefficient (Fig. 9b) suggest that \( t_\text{p} = 1 \). One can therefore estimate the hole concentration and mobility from the total conductivity and thermopower data by combining Eq. 1 and 2, neglecting the right side terms related to n-type electronic transport. The estimates of electron concentration can be obtained from the electroneutrality condition

$$2\delta + p = n \quad [3]$$

using the oxygen deficiency values determined by TGA. Increasing oxygen deficiency on reduction leads to the formation of n-type charge carriers, reflected by decreasing Seebeck coefficient. In these conditions, the values of \( \mu_\text{p}, \mu_\text{n}, p, n \), and \( t_\text{p} \) can be derived using Eq. 1-3 in combination with the iron disproportionation constant

$$K_d = np \quad [4]$$

Typical results of such estimations are presented in Fig. 10a and b. As expected, the \( \mu_\text{p} \) values are substantially higher than \( \mu_\text{n} \) and decrease on reducing \( p(O_2) \) due to raising local distortions induced by oxygen deficiency. The estimated hole mobility in air, 0.05–0.13 cm² V⁻¹ s⁻¹ at 1023–1223 K, is close to the characteristic threshold of 0.1 cm² V⁻¹ s⁻¹, considered to separate broadband and small-polaron conduction. This fact, and the decrease in \( \mu_\text{p} \) values on heating, may argue in favor of the band mechanism. The estimated mobility of n-type charge carriers is lower than 8 \( \times 10^{-4} \) cm² V⁻¹ s⁻¹ and is temperature-activated, indicative of polaron hopping. In addition, the apparent activation energy for the

### Table III. Average linear thermal expansion coefficients of Ca(Fe,Cr)₂O₄₋₄ ceramics.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Method</th>
<th>( T ) (K)</th>
<th>Atmosphere</th>
<th>( \text{TEC} \times 10^6 ) (K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaFe₂O₄</td>
<td>Dilatometry</td>
<td>973–1223</td>
<td>Air</td>
<td>13.9 ± 0.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>923–1223</td>
<td>Ar–O₂</td>
<td>13.8 ± 0.1</td>
</tr>
<tr>
<td>CaFe₂O₄</td>
<td>XRD</td>
<td>298–1373</td>
<td>Air</td>
<td>12.9 ± 0.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>873–1373</td>
<td>Air</td>
<td>13.9 ± 1.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>298–1173</td>
<td>Vacuum</td>
<td>10.8 ± 0.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>873–1173</td>
<td>Vacuum</td>
<td>9.6 ± 0.7</td>
</tr>
<tr>
<td>CaFe₁.₅Cr₀.₅O₄</td>
<td>Dilatometry</td>
<td>923–1223</td>
<td>Air</td>
<td>12.31 ± 0.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>923–1223</td>
<td>Ar–O₂</td>
<td>12.5 ± 0.3</td>
</tr>
</tbody>
</table>

\( ^a \) \( p(O_2) = 6 \times 10^{-4} \) atm.

\( ^b \) Total pressure in the range of 5 \( \times 10^{-8} \) to 5 \( \times 10^{-7} \) atm.

### Table IV. Apparent activation energies for oxygen ionic and electronic transport in CaFe₂O₄₋₄.

<table>
<thead>
<tr>
<th>Quantity (symbol)</th>
<th>( T ) (K)</th>
<th>( p(O_2) ), atm</th>
<th>( E_a ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total conductivity (( \sigma ))</td>
<td>653–923</td>
<td>0.21</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>923–1173</td>
<td>0.21</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>1193–1273</td>
<td>0.21</td>
<td>50</td>
</tr>
<tr>
<td>Oxygen ionic conductivity (( \sigma_0 ))</td>
<td>1123–1273</td>
<td>0.21</td>
<td>325</td>
</tr>
<tr>
<td>n-type electronic conductivity (( \sigma_n ))</td>
<td>1023–1173</td>
<td>10⁻⁵</td>
<td>129</td>
</tr>
<tr>
<td>Electron mobility (( \mu_\text{e} ))</td>
<td>1023–1173</td>
<td>10⁻⁵</td>
<td>122</td>
</tr>
</tbody>
</table>

**Figure 6.** Temperature dependencies of the unit cell parameters of CaFe₂O₄₋₄ equilibrated in air and at the total pressure of 5 \( \times 10^{-4} \) to 5 \( \times 10^{-7} \) atm.

**Figure 7.** Temperature dependencies of the total conductivity of CaFe₂O₄₋₄ and CaFe₁.₅Cr₀.₅O₄₋₄ ceramics in air, compared to the data on brownmillerite-type Ca₃Fe₂O₆₋₄.\(^{12}\)
electron mobility (Table IV) is significantly higher than expected for a small-polaron mechanism, thus confirming the conclusion 17 on the formation of stable defect clusters involving Fe$^{2+}$ cations and oxygen vacancies.

The latter conclusion is also validated by the weak dependence of oxygen transference numbers \(t_{O^-}\) on the oxygen partial pressure (Fig. 11), which results mainly from the variations of p-type electronic transport (Fig. 9). Such behavior indicates that the oxygen ionic conduction is essentially \(O_2\)-independent due to a low concentration of mobile vacancies, determined by the cluster dissociation processes. In combination with structural constraints, this factor is responsible for very low ionic conductivity of CaFe$_2$O$_{4−}\$ Fig. 8, whereas the activation energy (Table IV) is almost twice as high as the average oxygen-vacancy migration energy evaluated by the computer simulation studies, \(\approx 170\) kJ/mol.\(^{17}\) The oxygen fluxes through dense CaFe$_2$O$_{4−}\$ membranes placed under electrical and/or oxygen chemical potential gradients were time independent within the limits of experimental uncertainty; one typical example of the faradaic efficiency data is shown in the inset of Fig. 11. If calcium cationic transport would be significant, the oxygen fluxes should decrease with time owing to blocking of the electrodes (FE) or membrane surface (OP). Also, no traces of cation demixing caused by Ca$^{2+}$ conduction were revealed by the EDS analysis of CaFe$_2$O$_{4−}\$ ceramics tested under applied voltage and \(p(O_2)\) gradients during 300–1200 h, as illustrated by Fig. 12.

Behavior in reducing atmospheres.— Reducing \(p(O_2)\) below \(10^{-11}–10^{-16}\) atm at 1023–1223 K leads to a drastic increase of the total conductivity and Seebeck coefficient, followed by hysteresis phenomena on subsequent reoxidation (Fig. 13). Note that for the data on electrical properties in the vicinity of these hystereses, the equilibration times were as long as 25–60 h. The observed behavior is caused by CaFe$_2$O$_{4−}\$ Phase decomposition into Ca$_2$Fe$_2$O$_{5−}\$ and Fe$_3$O$_4$ on reduction, in agreement with XRD analysis (Fig. 1a).

**Figure 8.** Temperature dependencies of the oxygen nonstoichiometry and oxygen ionic conductivity of CaFe$_2$O$_{4−}\$ ceramics in air. The ionic conductivity was calculated from the data on total conductivity and oxygen ion transference numbers determined by the oxygen permeability and faradaic efficiency measurements. The inset shows one example of the OP data for 1.0 mm thick membrane.

**Figure 9.** Oxygen partial pressure dependencies of the total conductivity (a) and Seebeck coefficient (b) of CaFe$_2$O$_{4−}\$.

**Figure 10.** Temperature dependencies of the electronic charge carrier concentrations \([k]\), mobilities \([\mu_k]\) and partial conductivities \([\sigma_k]\) in air and at \(p(O_2) = 10^{-5}\) atm, estimated from the total conductivity, Seebeck coefficient, and oxygen nonstoichiometry data (see text).
traces of CaFe$_3$O$_5$ phase visible in the XRD patterns of reduced CaFe$_2$O$_4$ appear due to kinetic reasons, namely, slow equilibration processes associated with a stagnated cation diffusion; the same reason is responsible for the conductivity hysteresis on reoxidation.

At 1223 K, the decomposition of CaFe$_2$O$_4$ occurs at oxygen chemical potentials close to the hematite $\leftrightarrow$ magnetite boundary in the binary Fe–O system, suggesting that this transition is induced by excessive lattice stress when the concentration of relatively large Fe$^{2+}$ cations increases. Most likely, a similar nature associated with CaFe$_2$O$_4$ lattice relaxation near the point defects is relevant for the tendencies to local structural distortions and defect clustering on reduction. Whatever the microscopic mechanisms, the redox stability of CaFe$_2$O$_4$ appears considerably lower with respect to perovskite-like ferrites, where the average oxidation state of iron may vary in a wide range without structural collapse and the reductive decomposition is accompanied with metallic Fe.

Figure 11. Oxygen-ion transference numbers of CaFe$_2$O$_4$, determined by the faradaic efficiency technique, as function of the oxygen pressure gradient. Inset shows one representative example of the time dependence of faradaic efficiency at 1173 K.

Figure 12. Comparison of the EDS spectra collected at the anode and cathode sides of CaFe$_2$O$_4$ ceramics after the faradaic efficiency tests under zero $p(O_2)$ gradient during more than 1100 h.

Figure 13. Example illustrating the variations of total conductivity (a) and Seebeck coefficient (b) of CaFe$_2$O$_4$ ceramics on reductive decomposition and subsequent reoxidation at 1173 K. Arrows show the direction of $p(O_2)$ changes.

Figure 14. Oxygen partial pressure dependencies of the total conductivity of CaFe$_2$O$_4$ on reduction at 1223 K, compared to the data on binary iron oxide ceramics.
revealed by static lattice simulations, this factor leads to low oxygen permeation and faradaic efficiency techniques vary in the p-type electronic charge carriers formed due to iron disproportionation. The predominant oxidation state of iron cations is 3+. The close to atmospheric, the conductivity of CaFe₂O₄−ₓ is as low as 0.0046–0.0059 at 973–1223 K and pressure dependencies of electrical properties, and literature data on Seebeck coefficient, oxygen permeability, and faradaic efficiency.

Figure 15 compares the approximate low-p(O₂) stability limits of CaFe₂O₄−ₓ, estimated from the oxygen partial pressure dependencies of electrical properties, and literature data on LaFeO₃−ₓ, CaFe₂O₅−ₓ and binary iron oxides.

Conclusions

Single-phase CaFe₂O₄−ₓ ceramics with density of >95% was prepared using the glycine-nitrate process and characterized by XRD, SEM/EDS, TGA, Mössbauer spectroscopy, controlled-atmosphere dilatometry, and measurements of the total conductivity, Seebeck coefficient, oxygen permeability, and faradaic efficiency. The thermogravimetric and Mössbauer spectroscopy studies showed that, in the oxygen partial pressure range where CaFe₂O₄−ₓ phase exists, the predominant oxidation state of iron cations is 3+. The oxygen deficiency of CaFe₂O₄−ₓ is as low as 0.0046–0.0059 at 973–1223 K and p(O₂) = 10⁻⁹–0.21 atm. In combination with structural constraints and strong tendency to the formation of stable defect clusters involving oxygen vacancies and Fe²⁺ cations, prevented by static lattice simulations, this factor leads to low oxygen-ionic and n-type electronic transport. At oxygen pressures close to atmospheric, the conductivity of CaFe₂O₄−ₓ is governed by the p-type electronic charge carriers formed due to iron disproportionation. The oxygen ion transference numbers determined by the oxygen permeation and faradaic efficiency techniques vary in the range (0.2–7.2) × 10⁻⁴ at 1123–1273 K in air. No evidence of any significant cationic contribution to the total conductivity was found. Decreasing oxygen chemical potential results in a modest contraction of orthorhombic CaFe₂O₄−ₓ lattice and in the transition to dominating n-type electronic conduction, followed by decomposition. The approximate phase stability limits estimated by the electrical measurements lie between those of CaFe₂O₅−ₓ brownmillerite and the hematite/magnetite boundary in binary Fe–O system. The average thermal expansion coefficients of CaFe₂O₄−ₓ ceramics, calculated from the dilatometric and high-temperature XRD data, are 9.6 to 13.9 × 10⁻⁶ K⁻¹ in the oxygen partial pressure range from 10⁻⁸ to 0.21 atm at 873–1373 K. Although the dimensional stability of CaFe₂O₄−ₓ on reducing p(O₂) might be of significant interest, the applicability of this compound for high-temperature electrochemical devices is very limited due to poor transport properties. The structure of CaFe₂O₄−ₓ comprising edge-shared FeO₆ octahedra may not tolerate extensive acceptor-type doping, increasing oxygen deficiency, and incorporation of larger cations in the calcium sites. In particular, the solubility of lower-valence cations, such as Co and Ni, is considerably lower than 25% of the iron site concentration. Doping with 25 mol % chromium leads to a moderately lower thermal expansion and higher chemically induced contraction and has a negligible effect on the total conductivity at elevated temperatures.

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