



Ceramic and transport properties of halogen-substituted strontium ferrite

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ABSTRACT

An attempt of fluorine and chlorine substitution for oxygen in strontium ferrite $\text{SrFeO}_{3-\delta}$ was undertaken in search of a new means of influence on the oxide properties. An uncontrollable removal of halogen-ions from oxides during synthesis was detected. Nevertheless, residual halogens were found to provide a notable impact on ion conductivity and oxide stability under reducing conditions. More than twice higher ion conductivity relative to $\text{SrFeO}_{3-\delta}$ was recorded in materials with nominal compositions $\text{SrFeO}_{2.8-\delta}\text{F}_{0.2}$, $\text{SrFeO}_{2.6-\delta}\text{Cl}_{0.4}$, and $\text{SrFeO}_{2.4-\delta}\text{Cl}_{0.6}$. The strong effect of halogen addition on ceramic properties of oxides was revealed. While $\text{SrFeO}_{3-\delta}$ was known for its poor sinterability, adding 0.2 mol of fluorine or chlorine during the synthesis of $\text{SrFeO}_{3-\delta}$ was shown to result in successful obtaining gas-tight ceramics.

1. Introduction

Oxides with mixed oxygen-ionic and electronic conductivity are widely used in various electrochemical processes, such as electricity generation, gas electrolysis, oxygen separation, catalysis, conversion of oil and gas into high-demanded products [1–3]. The applicability of oxides in the listed technologies is determined on the basis of compliance with a set of criteria for structural, thermodynamic, transport, mechanical and chemical properties. The task of achieving the target characteristics of oxides is solved by changing their composition. One of the most convenient matrices for such modifications is the perovskite structure, which provides a wide range of substitution models in the cation sublattices and thereby allows affecting the oxide properties. In some cases, the possibilities of cation substitution have been exhausted to a considerable degree by extensive research. In particular, a great number of works related to cation substitution in both A- and B- sublattice of strontium ferrite can be found [4–7].

The literature review has shown that anionic substitution may serve as a new effective means for changing functional characteristics of mixed conductors. For example, the inclusion of chlorine ions in the $\text{SrFeO}_{3-\delta}$ lattice matrix has been found to significantly enhance ethene selectivity and ethane conversion in the oxidative dehydrogenation of ethane [8]. A significant substitution effect of chlorine on the characteristics of the catalyst $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.2}\text{Co}_{0.8}\text{O}_{3-\delta}$ in the oxidative coupling of methane to C_2H_6 and C_2H_4 has been detected [9]. Some authors have revealed that fluorine substitution improves electrochemical and thermal properties of cathode $\text{LiM}_{0.05}\text{Co}_{0.95}\text{O}_{1.95}\text{F}_{0.05}$ ($\text{M} = \text{Mg}, \text{Al}, \text{Zr}$)

[10]. An increased chemical stability of proton electrolytes in relation to CO_2 as a result of substitution of fluorine, chlorine, and bromine in $\text{BaCe}_{0.9}\text{Gd}_{0.1}\text{O}_{3-\delta}$ has been noted [11]. Other authors, studying proton conductors, have revealed an increase in proton and oxygen-ion conductivity of $\text{Ba}_2\text{In}_2\text{O}_5$ resulting from partial oxygen substitution by fluorine [12]. Another study has reported about chlorine-substituted oxygen membrane based on $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$, which at moderate temperatures demonstrates improved oxygen permeability [13]. A number of possible reasons for the observed effects are regarded, such as a reduction of the binding energy of oxygen with the lattice [13], a decrease of oxygen vacancy concentration [14], a change in d-cation oxidation state, an increase in oxygen ion mobility [15] etc. Nevertheless, some authors, considering the causes of the observed effects, note that their arguments are only a preliminary speculation, while a profound research is required in order to elucidate the mechanisms of halogen influences [11].

Thus, one can claim that anionic substitution, as a new technique for modifying properties of mixed conductors, has been successfully tested. An impact of the new tool on the most important characteristics of materials for high-temperature electrochemical applications has been convincingly demonstrated. At the same time, the majority of studies mentioned have narrow practical orientation, while the potential of the anionic substitution deserves a comprehensive study.

This work is aimed at studying the influence of anionic substitution on the structure, stability, ionic and electronic transport of strontium ferrite $\text{SrFeO}_{3-\delta}$. A specific characteristic of this oxide is a phase transition into the brownmillerite structure at high concentrations of

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oxygen vacancies. So, verification of the possibility to stabilize the cubic structure by partial filling of oxygen vacancies by halogen ions is one of the tasks of this work.

2. Experimental

Halogen-substituted oxides with nominal compositions of $\text{SrFeO}_{3-x}\text{F}_x$ (0, 0.2, 0.4, 0.6) and $\text{SrFeO}_{3-x}\text{Cl}_x$ (0.2, 0.4, 0.6), which are further referred to as SFF_x and SFC_x , respectively, were synthesized by self-combustion method with the use of high-purity reagents Fe, SrCO_3 , SrF_2 and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$. The required amount of primary materials was dissolved in nitric acid. Then glycine in a molar ratio of 2:1 to nitrates was added to the solution, the mixture was heated until water evaporation and auto-ignition. The obtained intermediate product was ground and annealed in air at a temperature of 900 °C for 10 h. The ceramic substances, thus purified from residuals of organics and carbon, were subjected to milling and pressing into discs with a diameter of 20 mm. Discs of chlorine-containing strontium ferrite were sintered at 1000 °C for 10 h, fluorine-containing ones – at 1200 °C for 10 h. Rectangular bars of $12 \times 2 \times 2$ were cut from the obtained ceramic discs to be used for measuring electrical conductivity.

The phase composition and crystalline structure of sintering products were controlled by Shimadzu XRD-7000 diffractometer in CuK_α radiation. The PCW software was employed for structural refinement. The morphology of ceramics was characterized using JEOL JSM 6390-LA scanning electron microscope. The thermogravimetric measurements were carried out with SETARAM TG-92 thermoanalyzer in the mode of cooling in air from 950 °C to 100 °C at a rate of 1 °C/min. The measurements of electrical conductivity were performed by a four-probe dc technique in the range of oxygen partial pressure (p_{O_2}) from 10^{-15} atm to 0.5 atm at 950 °C for all compositions, and in the range of p_{O_2} from 10^{-19} atm to 10^{-7} atm at 750–950 °C for oxides with maximal conductivity. An electrochemical cell made of YSZ ceramics, equipped with an oxygen pump and sensor, was employed to maintain and control the partial pressure of oxygen over the sample. The measurements were carried out in isothermal runs in the mode of decreasing partial oxygen pressure. The equilibration criterion at given values of temperature and oxygen pressure was selected equal to variations in the logarithm of conductivity less than 0.0001 per minute. Additional experimental details can be found elsewhere [16]. The stability limits for composition $\text{SFF}_{0.2}$ under reducing conditions were evaluated using the same experimental setup. When the electrical conductivity measurements were accomplished, additional measuring runs were performed down to extremely low p_{O_2} until a sharp drop in σ values was observed, thus indicating the incipient decomposition of the material. This approach was successfully employed earlier [17,18].

3. Results and discussion

3.1. Structure and morphology

The results of X-ray powder diffraction for $\text{SrFeO}_{3-\delta}$, SFF_x and SFC_x , presented in Fig. 1, are indicative of the formation of single-phase compositions with tetragonal structure (S.G. $I4/mmm$). Unit cell parameters of materials are summarized in Table 1. The insert in Fig. 1 demonstrates the variation of calculated perovskite cell parameter, under increasing anion substitution degree. Though a general trend for unit cell parameters to increase gives evidence of halogen ion incorporation in anion sublattice, non-systematic parameter variation may suggest that partial removal of chlorine and fluorine occurs during the synthesis. The problem of oxyhalide instability at high temperatures is unpopular lately. Development of fluorination technique by reaction with poly(vinylidene fluoride) at 400 °C in a great measure solved the problem for materials, focused on the low-temperature use [19,20]. Since an improvement of high-temperature characteristics of oxides by halogenation makes only sense for stable materials, there are attempts

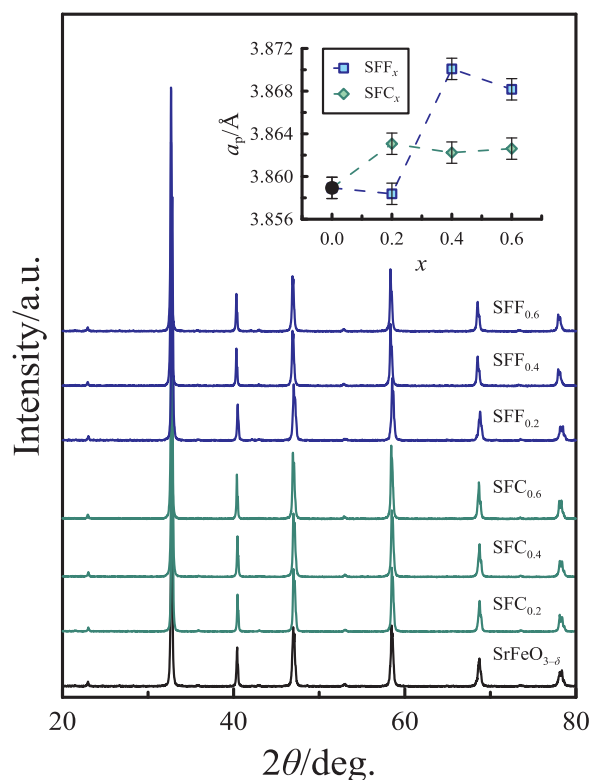


Fig. 1. Room-temperature X-ray powder diffraction patterns for $\text{SrFeO}_{3-\delta}$, SFF_x and SFC_x . The insert represents the variation of perovskite unit cell parameter, calculated from data in Table 1, as a function of the nominal content of a halogen.

Table 1

The unit cell parameters (SG $I4/mmm$) and activation energy for ion and electron conductivity of halogen-substituted $\text{SrFeO}_{3-\delta}$.

Composition	$a/\text{\AA}$	$c/\text{\AA}$	E_i/eV^a	E_e/eV^b	E_n/eV
$\text{SrFeO}_{3-\delta}$	10.932(2)	7.701(9)	0.26	2.5	2.2
$\text{SFF}_{0.2}$	10.931(3)	7.698(1)	0.49	2.3	2.5
$\text{SFF}_{0.4}$	10.953(1)	7.726(5)			
$\text{SFF}_{0.6}$	10.946(4)	7.733(5)			
$\text{SFC}_{0.2}$	10.940(8)	7.705(8)			
$\text{SFC}_{0.4}$	10.937(9)	7.704(8)	0.30	2.1	2.2
$\text{SFC}_{0.6}$	10.936(7)	7.708(8)			

^a high-temperature region.

^b low-temperature region.

to demonstrate such stability. For instance, temperature-programmed desorption of fluorine from $\text{SrFeO}_{2.95-\delta}\text{F}_{0.05}$ and $\text{SrFeO}_{2.9-\delta}\text{F}_{0.1}$ powders in argon flow and the qualitative determination of emitted F_2 gas with a mass spectrometer was performed in [21]. Authors detected no change of signal related to fluorine concentration in response to an increase in specimen temperature from 200 °C to 1000 °C and attributed the result to the stability of materials. Actually, this result should not be taken as evidence of material stability, but only an indicator that molecular fluorine cannot be released from oxyfluorides, while other mechanisms may be responsible for degradation. A convincing examination of high-temperature stability of oxyhalides was carried out in [22]. The studying materials were intended for use as catalysts for oxidative coupling of methane, so they were tested under operating conditions at 750 °C during 8 h. The F, Cl, and Br compositions of the catalysts were found to be decreased from 4.0 to 3.7 wt%, 7.0–5.6 wt%, and 14.2–9.8 wt%, respectively. The F^- ions demonstrated to be more resistant to leaching than the Cl^- or Br^- ions. According to the authors' opinion, halogen loss occurs due to H_2O interactions with halide ions to produce HX which escape at high temperatures. In our case, partial

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