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Synthesis and characterization of perovskite-type $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$ ($0.63 \leq x < 1.0$) and $\text{Sr}_{0.75}\text{Y}_{0.25}\text{Fe}_{1-y}\text{M}_y\text{O}_{3-\delta}$ ($M=\text{Cr}, \text{Mn}, \text{Ni}$), ($y=0.2, 0.33, 0.5$)

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ABSTRACT

Oxygen-deficient ferrates with the cubic perovskite structure $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$ were prepared in air ($0.71 \leq x \leq 0.91$) as well as in N_2 ($x=0.75$ and 0.79) at 1573 K. The oxygen content of the compounds prepared in air increases with increasing strontium content from $3-\delta=2.79(2)$ for $x=0.75$ to $3-\delta=2.83(2)$ for $x=0.91$. Refinement of the crystal structure of $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$ using TOF neutron powder diffraction (NPD) data shows high anisotropic atomic displacement parameter (ADP) for the oxygen atom resulting from a substantial cation and anion disorder. Electron diffraction (ED) and high-resolution electron microscopy (HREM) studies of $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$ reveal a modulation along $\langle 1\ 0\ 0 \rangle_p$ with $G \pm \sim 0.4 \langle 1\ 0\ 0 \rangle_p$ indicating a local ordering of oxygen vacancies. Magnetic susceptibility measurements at 5–390 K show spin-glass behaviour with dominating antiferromagnetic coupling between the magnetic moments of Fe cations. Among the studied compositions, $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$ shows the lowest thermal expansion coefficient (TEC) of 10.5 ppm/K in air at 298–673 K. At 773–1173 K TEC increases up to 17.2 ppm/K due to substantial reduction of oxygen content. The latter also results in a dramatic decrease of the electrical conductivity in air above 673 K. Partial substitution of Fe by Cr, Mn and Ni according to the formula $\text{Sr}_{0.75}\text{Y}_{0.25}\text{Fe}_{1-y}\text{M}_y\text{O}_{3-\delta}$ ($y=0.2, 0.33, 0.5$) leads to cubic perovskites for all substituents with $y=0.2$. Their TECs are higher in comparison with un-doped $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$. Only $M=\text{Ni}$ has increased electrical conductivity compared to un-doped $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$.

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1. Introduction

Perovskite-related oxides ABO_{3-y} with d-electron-rich transition metal B-cations like Mn, Fe, Co and Ni are considered as materials for oxygen reduction in various high-temperature electrochemical devices such as cathodes in solid oxide fuel cells (SOFCs). Manganates like Sr substituted LaMnO_3 (LSM) combine reasonable conductivity with thermodynamic stability. They are therefore standard cathode materials in SOFCs with YSZ ($\text{Zr}_{1-x}\text{Y}_x\text{O}_{2-x/2}$) electrolyte operated at high temperature [1].

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Perovskites with Fe and Co, which exhibit high oxide-ion conductivity due to a lower B–O bonding energy and easy transition between different coordination polyhedra, are less stable. However, they combine high electronic with high oxide-ion conductivity and can be used as cathode materials in intermediate-temperature SOFC (IT-SOFC) due to changes in the mechanism of oxygen reduction in comparison with LSM which exhibits negligible oxide-ion conductivity [2]. Cobaltates, like strontium-doped LaCoO_3 (LSC), show superior oxide-ion and electronic conductivity but suffer from high TEC (> 20 ppm/K) due to a temperature-induced spin transition between low and high spin states of Co^{3+} [3,4]. Perovskite-like ferrates exhibit one order of magnitude lower conductivity at high temperatures in comparison with the cobaltates. Thus, the conductivities of $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-y}$ and

$\text{Pr}_{0.8}\text{Sr}_{0.2}\text{FeO}_{3-y}$ at 1073 K are ~ 110 S/cm [5] and 78 S/cm [6], respectively, which are much lower in comparison with $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_{3-y}$ (1300 S/cm at 1073 K [7]) and $\text{Pr}_{0.85}\text{Sr}_{0.15}\text{CoO}_{3-y}$ (~ 1100 S/cm at 973 K [8]), however, high enough for use as cathode materials in SOFCs. The much lower price for Fe oxides than for Co, Mn and Ni ones, makes ferrates prospective cathode materials in SOFCs [9]. Recently cubic perovskite $\text{Sr}_{0.9}\text{K}_{0.1}\text{FeO}_{3-\delta}$ was successfully prepared and tested as cathode material in IT-SOFC [10,11].

$\text{Sr}_x\text{M}_{1-x}\text{FeO}_{3-\delta}$ (M —trivalent cation like Y or rare-earth cation) are known to exhibit various perovskite-related structures depending on the preparation conditions, like temperature and oxygen partial pressure. This result can be explained by the easiness in oxidizing Fe^{3+} to Fe^{4+} during a synthesis in oxidizing atmosphere. Thus Yo et al. reported a study of $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$, $x=0.25, 0.5$ and 0.75 prepared in air at 1473 K [12]. A cubic perovskite with $a=3.872$ Å was found for $x=0.75$, while orthorhombically distorted GdFeO_3 -type perovskite phases were reported for $x=0.25$ and 0.5 . Bréard et al. [13] found a smaller unit cell parameter ($a \approx 3.837$ Å) for $\text{Sr}_{0.8}\text{Y}_{0.2}\text{FeO}_{3-\delta}$ prepared at 1473 K under vacuum. In Ref. [14] no single-phase sample was obtained for $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{3-\delta}$ synthesised in air at 1373 K, while Abakumov et al. succeeded in preparing a single-phase ferrate $\text{Sr}_{0.75}\text{Y}_{0.25}\text{Fe}^{3+}\text{O}_{2.625}$ in vacuum at 1373 K [15]. Their X-ray powder diffraction (XRPD) study indicated the formation of ideal cubic perovskite phase, while electron diffraction revealed a tetragonal perovskite-related structure with $a \approx 2\sqrt{2} \times a_{\text{per}}$, $c \approx 4 \times a_{\text{per}}$. This crystal structure contains ordered A-cations and oxygen-vacancies and is closely related to that of $\text{Sr}_{0.75}\text{Y}_{0.25}\text{CoO}_{2.62}$ (314-phase below) [16,17]. Cubic perovskites $\text{Sr}_{0.67}\text{R}_{0.33}\text{FeO}_{3-\delta}$, $R=\text{Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er, Yb, and Y}$ were prepared by Battle et al. [18] in air at 1573 K, with unit cell dimensions slightly varying depending on the cooling conditions. For $R=\text{Y}$ a cubic perovskite phase with $a=3.866$ Å (oxygen content $3-\delta=2.77$) was reported when the sample had been slowly cooled down to room temperature, whilst a slightly larger unit cell $a=3.872$ Å (oxygen content $3-\delta=2.69$) was reported for a quenched sample. This is in contrast to what observed by Azad et al. [19] who reported a tetragonal perovskite phase $\text{Sr}_{0.67}\text{Y}_{0.33}\text{FeO}_{2.662}$ ($a \approx a_{\text{per}}$, $c \approx 3 \times a_{\text{per}}$) with layered ordering of Sr^{2+} and Y^{3+} in a sample made in air at 1233 K followed by annealing in oxygen at 673 K.

To our knowledge, high-temperature properties of ferrates $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$, which are important for their use as cathode materials in IT-SOFC like thermal expansion and electrical conductivity, have not been reported so far. In this work we present the synthesis, crystal structure study, thermal expansion behaviour and high-temperature electrical conductivity of perovskite-type oxides $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$ ($0.63 \leq x \leq 1.0$) and $\text{Sr}_{0.75}\text{Y}_{0.25}\text{Fe}_{1-y}\text{M}_y\text{O}_{3-\delta}$ ($M=\text{Cr, Mn, Ni}$), ($y=0.2, 0.33, 0.5$) prepared both in air and N_2 . We also report additional characterization of the prepared compounds like their magnetic properties.

2. Experimental

Samples of $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$, $0.63 \leq x < 1.0$ were prepared by heating stoichiometric amounts of pre-dried SrCO_3 (Mallinckrodt Chemical Works, 99.6%), Y_2O_3 (Davison Chemical Co., 99.9%) and Fe_2O_3 (ABCR GmbH, 99.8%). Appropriate amounts of mixed powder were ball-milled in a 45 ml plastic container with 10 ml *iso*-propanol, using Si_3N_4 milling balls (weight ratio powder/balls=1:2), for 50 min at 300 rpm. The milled powders were dried and ground in a mortar. Syntheses were carried out in air by heating pelletized samples to 1573 K at a rate of 300 K/h, held there for 12 h, and then cooled to 573 K at a rate of 300 K/h.

A separate batch of pellets was also prepared in N_2 following the same heating procedure.

Samples of $\text{Sr}_{0.75}\text{Y}_{0.25}\text{Fe}_{1-x}\text{M}_x\text{O}_{3-\delta}$ ($M=\text{Ni, Cr, Mn}$), ($x=0.2, 0.33, 0.5$) were prepared from stoichiometric amounts of SrCO_3 , Y_2O_3 , Fe_2O_3 and the appropriate oxide (NiO 99% pure; MnO_2 99.5% pure or Cr_2O_3 99.999% pure) ball-milled by the procedure described above. Pelletized samples were placed in a platinum crucible and heated in air at the rate of 250 K/h to 1573 K. The samples were annealed at 1573 K for 12 h and cooled down to ambient temperature at 300 K/h. For the synthesis in N_2 , pellets of intimately mixed initial reagents, obtained by the same procedure given above, were placed on a platinum foil inside an alumina boat and heated in flowing N_2 at the rate of 300 K/h to 1573 K. Before achieving final annealing temperature, the system was evacuated twice at 1373 K to remove any products of the reaction (such as carbon dioxide) and refilled with N_2 . Thereafter, the temperature was raised to 1573 K and the samples were annealed for a further 12 h and then cooled down to 973 K at 200 K/h, whereupon the furnace power was shut down and the samples left to cool down to room temperature.

Phase purity was checked by XRPD using a PANalytical X'Pert PRO MPD diffractometer equipped with a PIXCEL detector, $\text{CuK}\alpha 1$ radiation, variable slits with a constant 20×12 mm² area illuminated, step size 0.0167° , in the 2θ range 10 – 90° , with a total measuring time of 1 h. In order to obtain accurate unit cell parameters, Si was added as an internal standard. Unit cell parameters were determined using the Rietveld method using the FullProf program [20].

Time-of-flight (TOF) NPD data for $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$ were collected at room temperature using the GEM diffractometer [21] at the ISIS pulsed spallation neutron source, Rutherford Appleton Laboratory, UK. Approximately 8 g of sample were loaded into a thin-walled cylindrical vanadium can and mounted on an automatic sample changer. Prior to data analysis, data were normalised using an incoherent scattering pattern from a vanadium sample. Refinement the crystal structure was performed by the General Structure Analysis System, GSAS [22].

ED and HREM studies were made with a JEOL JEM2100F transmission electron microscope (TEM) with a Schottky-type field emission gun, equipped with a double tilt sample holder, operating at 200 kV.

Cerimetric [23,24] potentiometric titration was used to determine the oxygen content. In this method Fe^{4+} presented in the sample is comproporionated in acidic solution with an excess of Fe^{2+} . The remaining Fe^{2+} is titrated by solution of Ce^{4+} with known concentration. For the titration about 25 mg of sample was dissolved in 50 ml of 1–2.5 M aqueous solution of HCl, containing 40 mg of $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. Unreacted Fe^{2+} was titrated with a 0.025 M solution of $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$. The concentration of the HCl solution used was found to be crucial. At low concentrations of HCl it was difficult to dissolve the samples, while at high concentrations fast oxidation of Fe^{2+} by O_2 from air was observed. The accuracy of the determination of the fraction of Fe^{4+} was estimated to be $\pm 1\%$. The cation compositions of the samples were checked using a JEOL JSM 74001-F SEM, operated at an accelerating voltage of 20 kV, equipped with an Oxford INCA energy dispersive X-ray (EDX) spectrometer. About 10 EDX point analysis were made on polished sample surfaces of each sample using a fixed oxygen stoichiometry used for the inter-element corrections.

The oxygen content was determined by a standard combustion method using a LECO TC444 apparatus. In this method a sample is fused in a high-purity graphite crucible at temperatures up to 3273 K in an inert gas. Oxygen is detected by infrared (IR) spectroscopy either in the form of CO_2 , CO or both, released as products of chemical interaction between oxide and graphite.

The accuracy of the results was checked by oxygen content determination of a standard with known oxygen content.

Thermogravimetric (TG) analyses were made using a PerkinElmer TGA7 instrument. Thermal expansion was measured with a Netzsch TMA 402 dilatometer in air at 313–1173 K and using a heating rate of 5 K/min. For the thermal expansion measurements, the powder samples were pressed into pellets with 8 mm diameter and 5–7 mm height and annealed at 1573 K for 12 h.

The conductivity measurements were performed in air in the temperature range 373–1073 K using the Van der Pauw setup in a ProboStat (Norecs) cell using ceramic disks of 20 mm diameter and 1–2 mm thickness. The AC impedance data in the frequency range 0.01 to 10^5 Hz was collected using a Solatron 1260 impedance analyser. Conductivity values ($1/\Omega$) for all samples as a function of temperature were obtained from the low frequency region < 1 Hz or DC conductivity plateaux in the Y' spectrum.

AC and DC magnetization measurements were performed in a Quantum Design MPMS-XL SQUID magnetometer. The temperature dependence of the magnetization (M) was studied between 5 K and 390 K, following two different protocols; zero-field-cooled (ZFC) and field-cooled (FC). The ZFC magnetization was obtained by cooling the sample to 5 K in zero field, turning on a weak magnetic field $H=4$ kA/m and measuring the magnetization as the sample warmed up. The FC magnetization was subsequently obtained by measuring the magnetization, in the same applied field, as the sample cooled down to 5 K.

3. Results

3.1. Crystal structure of $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$, $0.63 \leq x < 1.0$

Samples of $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$, $0.63 \leq x < 1.0$ were prepared in air and N_2 at 1573 K for 12 h. All the samples were black after synthesis. Single-phase samples are obtained in air for $0.71 \leq x \leq 0.91$ and their XRPD patterns show sharp reflections and can be indexed using a primitive cubic unit cells. For samples with $x=0.63$ and 0.67, a mixture of the cubic perovskite phase and YFeO_3 was observed. The unit cell parameter of $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$, $0.71 \leq x \leq 0.91$ prepared in air slightly increases with increasing strontium content (see Fig. 1) and their oxygen content, as determined by chemical titration, increases nearly linearly (Fig. 2), as well. For example, the oxygen content of the $x=0.75$ sample is $3-\delta=2.787(5)$ and for the $x=0.91$ sample $3-\delta=2.827(5)$. The oxygen content of the $x=0.75$ sample was confirmed by combustion analysis, which resulted in the value of

Fig. 1. Unit cell parameter variation as a function of Sr content for $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$ ($0.71 \leq x \leq 0.91$) sintered in air and N_2 .

Fig. 2. Oxygen content of $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$ ($0.71 \leq x \leq 0.91$) samples prepared in air as a function of Sr content (x).

$3-\delta=2.80$. EDX analysis gave cation compositions within one e.s.d. of the nominal ones, e.g., for $x=0.75$, $\text{Sr}:\text{Y}=0.75(1):0.25(1)$. Calculated from chemical composition the average formal oxidation state of Fe in $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$, $0.71 \leq x \leq 0.9$ thus increases with decreasing Y content from +3.29 for the $x=0.71$ to +3.57 for the $x=0.91$ sample.

For the samples of $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$, with $0.63 \leq x < 1.0$ made in N_2 , single-phase cubic perovskite materials were observed only for $x=0.75$ and 0.79. The corresponding unit cell parameters are larger in comparison with those prepared in air (Fig. 1) due to the expectedly smaller oxygen content and, therefore, lower average oxidation state of Fe. It should be mentioned that due to the low Fe^{4+} content in these phases, we were not able to determine their precise oxygen content by cerimetric titration. For compositions with $x < 0.75$, the main phase was still cubic perovskite but the presence of an orthorhombic phase, similar to that reported in Ref. [18] for $\text{Sr}_{0.66}\text{Y}_{0.33}\text{FeO}_{2.69}$ annealed in Ar, was also detected in the XRPD patterns. Above the solid solution limit $x > 0.79$, the main phase was $\text{Sr}_2\text{Fe}_2\text{O}_5$ with the brownmillerite-type structure [25].

The TG study in air of the $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$ sample sintered in air shows that oxygen loss starts at ~ 673 K (Fig. 3a). The oxygen content of the phase decreases from 2.79 down to 2.69 at 1173 K. It should be mentioned that $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{3-\delta}$ sintered in N_2 takes up oxygen between ~ 623 K and ~ 773 K, followed by a reversible loss at higher temperatures, see Fig. 3b. XRPD of the samples after TG measurements confirmed the cubic perovskite cell and the absence of admixture phases.

3.1.1. Neutron powder diffraction study of $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$

The crystal structure of $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$ was refined using TOF NPD data from the four higher-angle data banks. The structural refinement results are presented in Table 1 and the observed, calculated and difference profiles for $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$ are given in Fig. 4. The background was refined using a linear interpolation function containing 36 variables. A close investigation of the diffraction data revealed very small shoulders on several peaks, see inset in Fig. 4, which were attributed to reflections from a cubic phase with a slightly smaller a -parameter. Its refined weight fraction and lattice parameter were 1.4(1)% and $a=3.8412(6)$ Å, respectively. The phase was included in the refinement as impurity with an assumed composition $\text{SrFeO}_{3-\delta}$.

Fig. 3. Temperature variation in air of the oxygen content of the Sr_{0.75}Y_{0.25}FeO_{2.79} sample prepared in air (a) and N₂ (b).

Table 1

Coordinates, occupancies and atomic displacement parameters (ADP) for Sr_{0.75}Y_{0.25}FeO_{2.79} refined from the NPD data (S.G. *Pm-3m*, $a = 3.86455(3)$ Å; $\chi^2 = 6.71$, $R_p = 0.03^*$; $R_{wp} = 0.04^*$).

Atom		ADP $100 \times (\text{\AA}^2)$							
	Site	X	y	z	Frac	U_{iso}	U_{11}	U_{22}	U_{33}
Sr/Y	1b	0.5	0.5	0.5	0.75/0.25	1.583(9)			
Fe	1a	0	0	0	1	0.590(5)			
O	3d	0.5	0	0	0.93		0.94(2)	5.35(2)	5.35(2)

* Values are given for bank 6 at 154.4θ.

Fig. 4. Observed, calculated and difference NPD patterns for Sr_{0.75}Y_{0.25}FeO_{2.79}. In inset, magnification of reflections shows the presence of "shoulders" which are attributed to the presence of a second cubic perovskite phase SrFeO_{3-y} with a slightly smaller a -parameter of 3.8412(6) Å.

The crystal structure of Sr_{0.75}Y_{0.25}FeO_{2.79} was refined using the cubic perovskite structure model, S.G. *Pm-3m*, $a = 3.86455(3)$ Å. Except for the shoulders mentioned above no extra peaks, nor splitting of reflections due to lower symmetry, were observed in the NPD pattern. A satisfactory refinement for all banks was obtained by constraining Sr/Y occupancies to the nominal values, 0.75 and 0.25, respectively. It should be mentioned that due to the similar neutron scattering lengths for Sr and Y (7.02 fm for Sr and 7.75 fm for Y [26]) it was not possible to refine their relative ratio. In addition, the occupancy of the oxygen position was fixed to the value obtained from the chemical titration results ($g = 0.93$) and was not refined. Refined isotropic ADP for oxygen was much higher than those for the cations ($U_{iso} = 0.041$ Å²). An improved fit with experimental data was obtained for a refinement in an

Fig. 5. The crystal structure of Sr_{0.75}Y_{0.25}FeO_{2.79} showing ADP ellipsoids obtained from Rietveld refinement of TOF NPD data.

anisotropic approximation for the ADP of oxygen. Observed unusually high anisotropic ADP for oxygen (Table 1) is a clear indicator of anion sublattice disorder. Fig. 5 shows the perovskite unit cell with oxygen ADP ellipsoids elongated in-plane perpendicular to the Fe–O bond. This indicates a large amount of Fe cations with CN < 6.

3.1.2. Electron diffraction and high-resolution microscopy (HREM) studies of Sr_{0.75}Y_{0.25}FeO_{2.79}

Representative SAED patterns of Sr_{0.75}Y_{0.25}FeO_{2.79} obtained along the $\langle 100 \rangle_p$ and $\langle 110 \rangle_p$ are shown in Fig. 6a and b, respectively. The strong Bragg reflections agree well with the cubic perovskite cell (*Pm-3m*) with $a_{per} \sim 3.8$ Å in addition, extra intensities are seen along $\langle 100 \rangle_p$ with $G \pm \sim 0.4 \langle 100 \rangle_p$ marked by arrows in Fig. 6a and b. This modulation is similar to that reported for Sr_{0.8}Y_{0.2}Co_{0.5}Fe_{0.5}O_{2.77} [13].

The high-resolution micrograph of a crystallite of Sr_{0.75}Y_{0.25}FeO_{2.79} along the $\langle 100 \rangle_p$ direction reveals the basic perovskite lattice, see Fig. 7 with insets, representing magnified areas with different thickness from the main image. The basic perovskite axes are shown in the main image. In the image contrast variations can be seen which correspond to the satellite reflections in the ED patterns. They occur as darker bands seen on Fig. 7b in the image less than one unit cell wide extending over some unit cells in the other direction. The distance between these bands is typically 2 to 3 perovskite unit cells, corresponding to 7.8 to 11.4 Å. (Naturally, these contrast variations give rise to the same satellite reflections in the FFT of the HREM image as in the

Fig. 6. Selected area electron diffraction patterns for $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$ along $\langle 100 \rangle_p$ (left) and $\langle 110 \rangle_p$ (right). Extra reflections related to short-range ordering are marked by arrows.

SAED). The local ordering observed in the HREM images might arise from small variations in oxygen contents, forming local structural units that resembles $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.625}$ with the 314-phase structure [15] but also the $\text{Sr}_{0.67}\text{Y}_{0.33}\text{FeO}_{2.662}$ phase [19] with ordered oxygen vacancies as well as Sr/Y ordering. HREM image simulations using two alternative models; (i) one with a double perovskite sub cell $a \approx a_{\text{per}}$, $c \approx 2 \times a_{\text{per}}$ with partial ordering of oxygen vacancies (50%) in every second layer of Fe atoms along the c -axis (i.e., at the equatorial positions for FeO_6) and (ii) one with alternating layers of Sr and Y atoms along the c -axis, show that it is not straightforward to settle the true origin of the contrast variations, specially as the structural variations also are present along the line of sight. The structure is most likely a mixture of both models mentioned above, where a partial ordering of the Sr and Y cations is combined with an ordering of oxygen vacancies. The correlation between the satellite reflections of this kind in the SAED and the oxygen content was reported for $\text{Sr}_{0.8}\text{Y}_{0.2}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_z$ where $z=2.77$ had additional substructure reflections but $z=2.67$ did not [13]. Ordering of Sr and Y cations cannot be excluded as it has been reported for $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.62}$ prepared under vacuum [15].

Upon longer exposure to the electron beam the modulation along $\langle 100 \rangle_p$ in the $\langle 110 \rangle_p$ pattern disappears and instead an ordering along $\langle 111 \rangle_p$ appears in the thicker parts of the crystallites, as indicated in the image. This ordering is better seen in the corresponding FFT image, insets (a) and (b) in Fig. 8 as extra reflections at $G \pm 0.5 \langle 111 \rangle_p$. This would imply that the sample might get slightly reduced under the beam and thus enhancing the ordering observed from the $\frac{1}{2} \langle 111 \rangle_p$ reflection.

3.2. Crystal structure of $\text{Sr}_{0.75}\text{Y}_{0.25}\text{Fe}_{1-y}\text{M}_y\text{O}_{3-\delta}$ ($M=\text{Ni}, \text{Cr}, \text{Mn}$), ($x=0.20, 0.33, 0.50$)

Phase analysis data for the samples prepared both in air and N_2 after heating at 1573 K for 12 h are given in Table 2a and b, respectively. Nearly single-phase samples (reflections from unidentified phases $<1\%$) were prepared in air for the whole studied compositional range only in the case of $M=\text{Mn}$. The unit cell parameter of the cubic perovskite phase $\text{Sr}_{0.75}\text{Y}_{0.25}\text{Fe}_{1-y}\text{M}_y\text{O}_{3-\delta}$ decreases with increasing Mn-content. The oxygen content for the $y=0.2$ sample determined by combustion analysis corresponds to the formula $\text{Sr}_{0.75}\text{Y}_{0.25}\text{Fe}_{0.8}\text{Mn}_{0.2}\text{O}_{2.80}$. Therefore, the average formal oxidation state for the B-cations in this compound is the same as in undoped $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$. Taking into account the decrease of the stability of oxidation state +4 with number of

Fig. 7. High-resolution electron micrograph of a crystallite of $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$. Marked areas of the crystal with (a) thinner and (b) thicker parts have been enlarged for clarity. The arrows indicate contrast variations due to local structural ordering.

d-electrons among 3d-elements, one can assume that Mn has oxidation state +4 in the prepared compounds or, in other words, it substitutes Fe^{4+} . The smaller ionic radius of Mn^{4+} ($r=0.53 \text{ \AA}$

Fig. 8. High-resolution electron micrograph of a crystallite along $\langle 110 \rangle_p$ with marked areas of (a) thinner and (b) thicker parts of the crystal. Reflections and the corresponding part in the crystal are marked with arrows.

Table 2

Phase analysis data for $\text{Sr}_{0.75}\text{Y}_{0.25}\text{Fe}_{1-x}\text{M}_x\text{O}_{3-\delta}$ ($M=\text{Cr, Mn, Ni}$), ($x=0.2, 0.33, 0.5$) prepared in air (A) and N_2 (B). Unit cell parameters (in Å) are given only for the perovskite phase present in the samples. Content of the phases is given in wt% as derived from Rietveld refinement of the corresponding multiphase XRPD patterns.

x	Phase analysis		
	Cr	Mn	Ni
(A)			
0.2	$a=3.8876$ Å, 97.5%; YFeO ₃ , 1.7%; Fe ₂ O ₃ , 0.8%	$a=3.8570$ Å	$a=3.8680$ Å, 94.7%; NiO, 3.4%; Y ₂ O ₃ , 1.9%
0.33	$a=3.8866$ Å, 88.7%; YFeO ₃ , 5.1%; SrCrO ₄ , 5.3%; Sr ₃ Cr ₂ O ₈ , 0.9%	$a=3.8477$ Å	$a=3.8746$ Å, 86.1%; NiO, 6.6%; Y ₂ O ₃ , 3.8%; RP ^a , 3.5%
0.5	$a=3.8850$ Å, 49.9%; YFeO ₃ , 16.5%; SrCrO ₄ , 18.1%; Sr ₃ Cr ₂ O ₈ , 14.6%; Y ₂ O ₃ , 0.9%	$a=3.8349$ Å	$a=3.8740$ Å, 31.3%; RP ^a , 57.8%; NiO, 10.5%; Y ₂ O ₃ , 0.6%
(B)			
0.2	$a=3.8783$ Å, 98.2%; YFeO ₃ , 1.8%;	$a=3.8803$ Å	$a=3.8922$ Å, 95.5%; Ni(m), 2.0%; Y ₂ O ₃ , 2.5%
0.33	$a=3.8788$ Å, 94.9%; YFeO ₃ , 4.6%; Fe ₂ O ₃ , 0.5%	$a=3.8765$ Å, 97.6%; Y ₂ O ₃ , 1.1%; Fe ₂ O ₃ , 1.3%	$a=3.9065$ Å, 67.4%; Ni(m), 5.9%; Y ₂ O ₃ , 3.5%; RP ^a , 23.2%
0.5	$a=3.8761$ Å, 94.2%; YFeO ₃ , 5.1%; Fe ₂ O ₃ , 0.7%	$a=3.8753$ Å, 96.2%; Y ₂ O ₃ , 1.6%; Fe ₂ O ₃ , 2.2%	$a=3.9088$ Å, 17.6%; RP ^a , 72.9%; Ni(m), 9.5%

^a RP=tetragonal phase $(\text{Sr,Y})_3(\text{Fe,Ni})_2\text{O}_{7-\delta}$ with the structure of $n=2$ Ruddlesden-Popper series.

[27]) compared to Fe^{4+} ($r=0.585$ Å [27]) explains the considerably smaller unit cell parameter for the Mn-substituted phases compared to $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{3-\delta}$ ($a=3.86455(3)$ Å) prepared under the same experimental conditions. In the case of synthesis in N_2 , where the formation of Mn^{4+} is not expected, single-phase samples of $\text{Sr}_{0.75}\text{Y}_{0.25}\text{Fe}_{1-y}\text{Mn}_y\text{O}_{3-\delta}$ can only be prepared for $y=0.2$. (Table 2b). The larger unit cell parameter of the perovskite cell for $\text{Sr}_{0.75}\text{Y}_{0.25}\text{Fe}_{0.8}\text{Mn}_{0.2}\text{O}_{3-\delta}$ prepared in N_2 , compared to that prepared in air, reflects the lower number of cations in oxidation state +4 due to a lower oxygen content. For Cr-containing samples, only $y=0.2$ can be prepared with a low amount of admixture phases (<3%) in air and N_2 (Table 2a and b). Combustion analysis of the oxygen content gives the composition $\text{Sr}_{0.75}\text{Y}_{0.25}\text{Fe}_{0.8}\text{Cr}_{0.2}\text{O}_{2.86}$ for the sample prepared in air,

which corresponds to an average oxidation state of +3.47 for the B-cations in comparison with +3.33 in undoped $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$. The octahedral environment is often preferred for Cr^{3+} in oxides and it is probable that it mainly substitutes Fe^{3+} . This leads to an introduction of additional oxygen in perovskite and partial oxidation of the rest of the Fe^{3+} to Fe^{4+} . The increased oxygen content leads to a larger unit cell parameter than for the un-substituted compound $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$ despite the increasing amount of Fe^{4+} . Samples with a higher amount of Cr ($y>0.2$) prepared in air are multiphase and contain an increasing amount of SrCrO_4 , indicating partial oxidation of Cr^{3+} to Cr^{6+} under these conditions. However, the amount of admixture phases is smaller (~5%) when inert atmosphere (N_2) is used. In the case of Ni-containing samples, $\text{Sr}_{0.75}\text{Y}_{0.25}$ -

$\text{Fe}_{1-y}\text{Ni}_y\text{O}_{3-\delta}$, only the samples with $y=0.2$ contained less than 5% of admixture phases when synthesised in air or N_2 (Tables 2a and b). The additional phase is NiO or Ni , indicating that the Ni content of the perovskite phase is slightly lower than nominal one. The larger unit cell parameter of the perovskite phase in the Ni-substituted samples in comparison with undoped $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$ is likely due to the presence of the large Ni^{2+} cation ($r(\text{Ni}^{2+})=0.70 \text{ \AA}$ instead of $0.645 \text{ \AA}$ for Fe^{3+} (HS)) [27]. Ni-containing samples with $y=0.5$, prepared in air as well as N_2 , contained as a main phase a tetragonal $n=2$ member of Ruddlesden–Popper (RP) series $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ similar to $\text{Sr}_{2.25}\text{Y}_{0.75}\text{Co}_{1.25}\text{Ni}_{0.75}\text{O}_{6.84}$ [28], see Table 2b. The unit cell parameters of this $(\text{Sr,Y})_3(\text{Fe,Ni})_2\text{O}_{7-\delta}$ compound depend strongly on the annealing atmosphere used: i.e., $a=3.8374 \text{ \AA}$, $c=19.787 \text{ \AA}$ for the $y=0.5$ sample prepared in air and $a=3.8621 \text{ \AA}$, $c=19.637 \text{ \AA}$ for the one made in N_2 . The higher amount of this phase in the $y=0.5$ sample prepared in N_2 , most probably is an effect of the lower oxidation state of the B-cations. A study of the composition and crystal structure of this RP phase is in progress and will be reported elsewhere.

3.3. High-temperature conductivity of $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$, $x=0.75, 0.83, 0.91$ and $\text{Sr}_{0.75}\text{Y}_{0.25}\text{Fe}_{0.8}\text{M}_{0.2}\text{O}_{3-\delta}$ ($M=\text{Cr, Mn, Ni}$)

Arrhenius plots of the conduction for $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$, $x=0.75, 0.83, 0.91$ ceramic samples sintered in air are presented in Fig. 9. At low temperatures $< 673 \text{ K}$ nearly linear temperature dependence or thermally-activated behaviour is observed. The nature of the conductivity seems to be polaron hopping between adjacent Fe cations. There is a clear trend of increasing conductivity with increasing amount of Fe^{4+} (strontium content). Thus $\text{Sr}_{0.91}\text{Y}_{0.09}\text{FeO}_{3-\delta}$ sample exhibits the highest conductivity of 182 S/cm at $\sim 623 \text{ K}$. However, at higher temperatures the conductivity decreases dramatically due to the decrease of charge carrier concentration (Fe^{4+}) caused by oxygen losses from crystal lattice at $T > 673 \text{ K}$ as it was found by TG measurements (see Fig. 3a). Thus, the conductivity of $\text{Sr}_{0.91}\text{Y}_{0.09}\text{FeO}_{3-\delta}$ is just 36 S/cm at 1073 K . Values of conductivity at 673 K and 1073 K for other

compositions are reported in Table 3. It should be noted that similar behaviour is observed for $\text{Ln}_{0.5}\text{M}_{0.5}\text{FeO}_3$, $\text{Ln}=\text{La, Nd}$ and Sm ; $M=\text{Ba, Sr}$ with a maximum conductivity approaching $\sim 70 \text{ S/cm}$ for $\text{Ln}=\text{La}$ at $\sim 723 \text{ K}$ [29].

Only the Ni-substituted $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{3-\delta}$ shows slightly higher conductivity in comparison with undoped compound (Fig. 10, Table 3). Substitution of Fe by Cr and Mn leads to a substantial decrease in the conductivity by nearly one order of magnitude at 673 K (Table 3). This trend is often observed among perovskites with 3d-metals, where an increase of conductivity occurs from Cr-, Mn- and Fe- to Co-containing perovskites and then decreases to Ni-containing ones. Thus, the conductivity of LaCrO_3 is 0.34 S/cm (970 K), LaMnO_3 – 81 S/cm (1000 K); LaFeO_3 – 0.1 S/cm (800 K); LaCoO_3 – 1000 S/cm (800 K); LaNiO_3 – 410 S/cm (900 K) [30–32].

3.4. Thermal expansion behaviour of $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$ and $\text{Sr}_{0.75}\text{Y}_{0.25}\text{Fe}_{1-x}\text{M}_x\text{O}_{3-\delta}$ ($M=\text{Ni, Cr, Mn}$)

The thermal expansion for all samples exhibits a low and a high temperature part, at $T < 673 \text{ K}$ and $T > 673 \text{ K}$, respectively. As an example, the thermal expansion curve for $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{3-\delta}$ is given in Fig. 11. The expansion shows a clear breakpoint at $\sim 673 \text{ K}$ and almost linear expansion below and above this temperature. The significant increase in the TEC from 10.5 ppm/K to 17.2 ppm/K above the breakpoint is clearly associated with the continuous reduction of Fe^{4+} ions due to loss of oxygen with increasing temperature, as shown by the TG measurements, see Fig. 3a. It should be noted that neither variation of Y content nor partial substitution of Fe by Cr, Mn or Ni changes this two-step behaviour. Calculated TECs at low and high-temperature parts of the dilatometric curves for different samples are given in Table 3. From this table it is clear that for $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$ samples, the TEC both for low and high-temperature parts decreases with increasing Y content. This can be explained by the lower amount of Fe^{4+} in $x=0.75$ sample compared with $x=0.83$ and 0.91 . It is also clear that partial substitution of Fe by Cr, Mn or Ni does not decrease TEC for $\text{Sr}_{0.75}\text{Y}_{0.25}\text{Fe}_{1-x}\text{M}_x\text{O}_{3-\delta}$ samples (Table 3).

3.5. Magnetic properties of $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$

The temperature dependence of the magnetic susceptibility ($\chi=M/H$) for $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$, $x=0.75, 0.79, 0.83, 0.87$ and 0.91 , is given in Fig. 12(a). The result for the $x=0.75$ sample treated in N_2 is included for comparison. Except for the sample treated in N_2 , the observed behaviour resembles that of a spin glass material with magnetic irreversibility developing, as evidenced by the divergence between the FC and ZFC susceptibility curves, at temperatures T_{irr} close to the cusp of the ZFC susceptibility curves. Except for the $x=0.75$ sample, T_{irr} decreases with decreasing concentration of Y. Moreover, the magnetic susceptibility increases with decreasing Y concentration, but is smaller in comparison to that reported for SrFeO_3 ; $\chi(\text{SI}) \sim 1.5\text{--}2 \times 10^{-2}$ at the Néel temperature [33,34]. Comparing the two $x=0.75$ samples, it is clear that the susceptibility of the sample treated in N_2 is much suppressed in comparison to the sample treated in air. A similar suppression of the susceptibility was also observed for the $x=0.79$ sample treated in N_2 . Fig. 12(b) shows the inverse of the FC susceptibility ($1/\chi_{\text{FC}}$) versus temperature. The effective magnetic moment μ_{eff} per Fe ion was derived by fitting a Curie–Weiss law $1/\chi_{\text{FC}}=(T-\theta_{\text{eff}})/C$ to the data in the temperature range $300\text{--}390 \text{ K}$; $\mu_{\text{eff}}=4.26, 4.05, 4.13$ and $4.45\mu_B$ for $x=0.79, 0.83, 0.87$ and 0.91 , respectively. The μ_{eff} values are smaller than the spin-only values for the high-spin configurations of Fe^{3+} and Fe^{4+} . The Curie–Weiss temperature θ_{eff} is negative for all samples. The $1/\chi_{\text{FC}}$ versus temperature curve for the $x=0.75$

Fig. 9. Temperature dependence of the electrical conductivity of $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$, $x=0.75, 0.83$ and 0.91 samples in air.

Table 3

Linear thermal expansion coefficients (TEC) for the studied samples (in ppm/K) and their conductivity (in S/cm) at 673 K and 1073 K.

Composition	First range	Second range	σ (673 K)	σ (1073 K)
$\text{Sr}_{0.91}\text{Y}_{0.09}\text{FeO}_{3-\delta}$	14.3 (373–673 K)	30.2 (773–1173 K)	164	36
$\text{Sr}_{0.83}\text{Y}_{0.17}\text{FeO}_{3-\delta}$	15.7 (373–673 K)	24.8 (773–1173 K)	100	20
$\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{3-\delta}$	10.5 (373–673 K)	17.2 (773–1173 K)	63	27
$\text{Sr}_{0.75}\text{Y}_{0.25}\text{Fe}_{0.8}\text{Cr}_{0.2}\text{O}_{3-\delta}$	14.8 (373–673 K)	22.1 (773–1173 K)	12	14 (973 K)
$\text{Sr}_{0.75}\text{Y}_{0.25}\text{Fe}_{0.8}\text{Mn}_{0.2}\text{O}_{3-\delta}$	12.1 (373–673 K)	18.0 (773–1173 K)	9	6
$\text{Sr}_{0.75}\text{Y}_{0.25}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$	14.0 (298–673 K)	24.8 (773–1173 K)	68	27

Fig. 10. Temperature dependence of the electrical conductivity of $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{3-\delta}$, $\text{Sr}_{0.75}\text{Y}_{0.25}\text{Fe}_{0.8}\text{Cr}_{0.2}\text{O}_{3-\delta}$, $\text{Sr}_{0.75}\text{Y}_{0.25}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$, $\text{Sr}_{0.75}\text{Y}_{0.25}\text{Fe}_{0.8}\text{Mn}_{0.2}\text{O}_{3-\delta}$ samples in air. **Fig. 11.** Thermal expansion curve for $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$ in air. The dashed lines show linear fit for low- and high-temperature ranges.

sample is not linear in the temperature range used for extracting the effective magnetic moment and μ_{eff} is therefore not given for this sample. A more detailed analysis of the magnetic properties will be published elsewhere.

4. Discussion

Ferrates $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$ with ideal cubic perovskite structure presented in this work can easily be prepared at 1573 K both

Fig. 12. (a) ZFC and FC susceptibility M/H versus temperature for $\text{Sr}_{1-x}\text{Y}_x\text{FeO}_{3-\delta}$ with $x=0.75, 0.79, 0.83, 0.89$ and 0.91 . The result for the $x=0.75$ sample treated in N_2 is included for comparison. (b) Inverse of the FC susceptibility $1/\chi_{\text{FC}}$ versus temperature. The applied field was $H=4$ kA/m.

in air and N_2 . The unit cell parameter of $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$ ($a=3.86455(3)$ Å) prepared in air at 1573 K is slightly smaller than that reported for 1473 K in air ($a=3.872$ Å) [12]. This is most probably due to a complex correlation between oxygen content and annealing history. $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$ with $0.71 \leq x \leq 0.91$ prepared in air contains large amounts of Fe^{4+} varying from 29% for the $x=0.71$ to 57% for the $x=0.91$ sample. In spite of the absence of superstructure reflections and splitting or broadening of the basic perovskite reflections observed on XRPD or NPD patterns of $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$, ED indicates ordering of oxygen vacancies at the local scale. This is not surprising taking into account the high concentration of oxygen vacancies and stability of different polyhedra for $\text{Fe}^{3+/4+}$. Refinement of the average structure of $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$ using NPD data shows unusually high and

anisotropic ADPs for the oxygen atom, indicating significant static displacements from the ideal position, suggesting that many of the Fe cations are in polyhedra with CN < 6. A detailed investigation of the local environment of Fe in $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$ by total scattering analysis is currently in progress. The $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$ perovskite may be defined, therefore, as an oxygen deficient perovskite with only short range ordering of the oxygen vacancies while the average long-range order and symmetry of ideal perovskite is maintained.

The oxygen content of $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$ can easily be varied by changing the annealing temperature and/or oxygen partial pressure. Thus, $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$ starts to lose oxygen at ~ 673 K and the weight loss is fully recovered on cooling in air. However, the oxygen loss with increasing temperature changes dramatically both conductivity and thermal expansion: e.g., the conductivity of $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$ decreases from 63 S/cm at 673 K to 27 S/cm at 1073 K and at the same time, the TEC increases from 10.5 ppm/K at ~ 673 K to 17.2 ppm/K at ~ 1073 K (see Table 3). This causes internal stresses in the ceramic samples and results in the formation of cracks. Therefore, the wide variation of the oxygen content and easiness to reduce the average oxidation state of Fe in $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$ leads to a decrease of conductivity and the increase of TEC at higher temperatures makes these materials unsuitable as cathode materials for SOFCs. One way to decrease oxygen loss with temperature could have been partial substitution of Fe by other transition metal cations with stable octahedral coordination like Cr or Mn. However, this leads to a substantial decrease of the conductivity as shown in Fig. 10 and does not decrease the TEC in the high temperature range (Table 3).

5. Conclusions

We have successfully prepared oxygen-deficient ferrates $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$ at 1573 K both in air ($0.71 \leq x \leq 0.91$) and N_2 ($x=0.75$ and 0.79). XRD data show the formation of ideal cubic perovskites with disordered arrangements of Sr/Y and O-vacancies. However, an ED and HREM study of the $x=0.75$ sample indicates ordering of oxygen vacancies at the local scale. TG studies show that the oxygen content of the samples varies substantially in a wide temperature range and, therefore, influences the TEC and electrical conductivity behaviour, which are important properties when new oxide materials are considered as cathodes in SOFC. Thus the TECs of $\text{Sr}_x\text{Y}_{1-x}\text{FeO}_{3-\delta}$ in air increase by nearly 70% at $T > 773$ K and, at the same time, electrical conductivity decreases due to the lower amount of Fe^{4+} . Partial substitution of Fe by other 3d-metal cations, as in the case of $\text{Sr}_{0.75}\text{Y}_{0.25}\text{Fe}_{1-y}\text{M}_y\text{O}_{3-\delta}$, $M=\text{Cr}, \text{Mn}, \text{Ni}$, $x=0.2, 0.33$ and 0.5 , leads to the preparation of nearly single-phase samples for all substituents with $y=0.2$. However, both the TEC and high-temperature electrical transport properties of the prepared materials suffer from oxygen losses at ~ 773 K and they do not exhibit lower TECs or higher conductivities in comparison with undoped $\text{Sr}_{0.75}\text{Y}_{0.25}\text{FeO}_{2.79}$.

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