Conductivity and redox stability of new perovskite oxides 
SrFe$_{0.7}$TM$_{0.2}$Ti$_{0.1}$O$_{3-\delta}$ ($TM = $ Mn, Fe, Co, Ni, Cu)

Peter I. Cowin $^b$, Rong Lan $^a$, Christophe T.G. Petit $^b$, Dongwei Du $^a$, Kui Xie $^d$, Huanting Wang $^c$, Shanwen Tao $^{a,c,*}$

$^a$ School of Engineering, University of Warwick, Coventry CV4 7AL, UK
$^b$ Department of Chemical & Process Engineering, University of Strathclyde, Glasgow G1 1XJ, UK
$^c$ Department of Chemical Engineering, Monash University, Clayton, Victoria 3800, Australia
$^d$ Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350109, China

Abstract

New perovskite oxides SrFe$_{0.7}$TM$_{0.2}$Ti$_{0.1}$O$_{3-\delta}$ ($TM = $ Mn, Fe, Co, Ni, Cu) were synthesised by sol-gel processes. Their redox stability and conductivity in both air and 5%H$_2$/Ar were investigated in detail. The cubic perovskite structure was also observed for all dopants with variation in the lattice parameters associated with different dopant environments and charge compensation mechanisms. Improvement of the electronic conductivity over SrFe$_{0.9}$Ti$_{0.1}$O$_{3-\delta}$ was observed for all dopants in air, attributed to increasing charge carrier concentrations. Reduction in 5%H$_2$/Ar exhibited minimal a material properties for SrFe$_{0.7}$Cu$_{0.2}$Ti$_{0.1}$O$_{3-\delta}$ with a significant reduction in conductivity was observed for SrFe$_{0.7}$Mn$_{0.2}$Ti$_{0.1}$O$_{3-\delta}$. All doped compounds exhibited a single phase cubic perovskite structure after reduction in 5%H$_2$/Ar at 700 °C with the exception of SrFe$_{0.7}$Ni$_{0.2}$Ti$_{0.1}$O$_{3-\delta}$ and SrFe$_{0.7}$Co$_{0.2}$Ti$_{0.1}$O$_{3-\delta}$ which displays secondary nickel and cobalt phases respectively upon reduction. SrFe$_{0.7}$Cu$_{0.2}$Ti$_{0.1}$O$_{3-\delta}$ is redox stable at a temperature below 700 °C and highly conductive with conductivities around 10 S cm$^{-1}$ in both air and reducing atmosphere which are about five times higher than those of pure SrFe$_{0.9}$Ti$_{0.1}$O$_{3-\delta}$. In terms of conductivity and redox stability, it is a potential redox stable electrode material for reversible and symmetrical solid oxide fuel cells as well.

© 2017 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

Redox-stable and conductive oxide materials are very useful in application in anode materials for solid oxide fuel cells (SOFCs). Development of redox stable anode for intermediate temperature solid oxide fuel cells (IT-SOFCs) is very important for use as electrode for reversible or symmetric solid oxide fuel cells [1–8]. The electrode materials for reversible and symmetric solid oxide fuel cells must be redox stable or redox reversible. They should exhibit high electrical conductivity in both air and reducing atmosphere [9–12]. In the reported redox stable oxides, SrFe$_{0.7}$Mn$_{0.2}$O$_{3-\delta}$ is an excellent material with electrical conductivity of 50 S cm$^{-1}$ at 850 °C in dry 5 vol% H$_2$/Ar [13]. This is slightly lower than those reported in the original report for Sr$_2$Fe$_{1.8}$Mn$_{0.2}$O$_{3.6}$ [14] although different conductivity values were also reported indicating the conductivity of the materials is very much related to the synthetic history [13]. SrFe$_{0.7}$Cu$_{0.2}$Ti$_{0.1}$O$_{3-\delta}$ based materials are promising electrodes for solid oxide fuel cells. It has been reported that Fe-dope doped SrTiO$_3$ with composition SrTi$_{0.9}$Fe$_{0.1}$O$_{3-\delta}$ and SrTi$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ exhibit good anode performance for SOFCs when combined with Ce$_{0.95}$Gd$_{0.05}$O$_2$ [15]. Research into B-site doped strontium ferrites has concentrated on stabilisation of the cubic perovskite structure. Doping with cations with a similar oxidation state has also shown to result in the formation of the cubic perovskite phase for SrFe$_{0.7}$Ni$_{0.2}$Ti$_{0.1}$O$_{3-\delta}$ through suppression of oxygen vacancy ordering [16–18]. This can be achieved through random distribution of dopant cations which either preferentially associate with oxygen vacancies [17] or which repulse oxygen vacancies [18]. Our previous research into titanium doped strontium ferrites, SrFe$_{1-x}$Ti$_{x}$O$_{3-\delta}$ (x ≤ 0.3) indicating SrFe$_{0.7}$Ti$_{0.1}$O$_{3-\delta}$ exhibits desired conductivity and redox stability, reduced thermal expansion coefficient compared to SrFe$_{0.9}$Ti$_{0.1}$O$_{3-\delta}$ which is a promising redox stable anode for IT-SOFCs [19]. SrFe$_{0.9}$Ti$_{0.1}$O$_{3-\delta}$ was also reported as a good cathode for SOFCs [20]. It has been reported that good performance has been achieved when Sr$_{1.08}$Fe$_{0.9}$Ti$_{0.1}$O$_{3-\delta}$ was used as electrode for SOFCs [21]. Cobalt-free perovskite oxide SrNb$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ was a good cathode for intermediate temperature solid oxide fuel cells [IT-SOFCs] [22]. In our previous study, it was posited that minimal doping of SrFe$_{0.9}$Ti$_{0.1}$O$_{3-\delta}$ with cations with a lower oxidation state could be utilised to improve the conductivity whilst retaining the redox stability [19]. To this end a series of transition metal (TM) doped strontium titanium ferrites, SrFe$_{0.7}$TM$_{0.2}$Ti$_{0.1}$O$_{3-\delta}$ (TM = Mn, Fe, Co, Ni, Cu), were synthesised and their stability and...
conductivity in oxidising and reducing atmospheres elucidated in this paper in order to explore their potential as electrode materials for SOFCs.

2. Experimental

2.1. Synthesis

SrFe$_{0.7}$TM$_{0.2}$Ti$_{0.1}$O$_{3-δ}$ (TM = Fe, Co, Cu, Mn, Ni) were produced by sol-gel processes. Stoichiometric amounts of Sr(NO$_3$)$_2$ (98%, Alfa Aesar) and Fe(NO$_3$)$_3$·9 H$_2$O (98%, Alfa Aesar) with either Co(NO$_3$)$_2$·6 H$_2$O (98%, Alfa Aesar), Cu(NO$_3$)$_2$·2.5 H$_2$O (ACS grade 98–102%, Alfa Aesar), MnC$_4$H$_6$O$_4$·4 H$_2$O (>99%, Sigma Aldrich) or Ni(NO$_3$)$_2$·6 H$_2$O (98%, Alfa Aesar) were dissolved in distilled water. A stoichiometric amount of titanium isopropoxide (C$_{12}$H$_{28}$O$_4$Ti) (97%, Alfa Aesar) was dissolved in ethanol and the solutions were combined, whilst maintaining a 2:1 ratio of ethanol to distilled water. Citric acid (99%, Alfa Aesar) was added in a 2:1 ratio to metal ions and the solution was heated until gelation. The resultant gel was fired at 600 °C for 2 h. A second firing at 1300 °C for 3 h was then performed. Pellets of all the samples (ø ≈ 13 mm × 2 mm) were uniaxially pressed at 221 MPa and sintered in air at 1300 °C for 2 h.

2.2. Analytical procedures

Phase purity and crystal parameters of the samples were examined by X-ray diffraction (XRD) analysis using a Bruker D8 Advance diffractometer (Cu K$_α$, radiation, $λ = 1.5405$ Å). GSAS [23] software was used to perform a least squares refinement of the lattice parameters of all the samples.

The densities of the pellets were determined from the measured mass and volume. Theoretical densities were calculated using experimental lattice parameters and the chemical formula SrFe$_{0.9}$Ti$_{0.1}$O$_{3-δ}$ and SrFe$_{0.7}$TM$_{0.2}$Ti$_{0.1}$O$_{3-δ}$ (TM = Co, Mn, Ni). The relative densities were calculated from the actual and theoretical density values. The density of the pellets was 75–85% for all compounds.

Thermal analysis was conducted using a Stanton Redcroft STA 1500 Thermal Analyser between room temperature and 800 °C with a heating/cooling rate of 10 °C min$^{-1}$ in either air or 5% H$_2$/Ar with gas flow rates of 50 mL min$^{-1}$.

2.3. Conductivity testing

The pellets (ø ≈ 13 mm × 2 mm) were coated on opposing sides using silver paste and fired at 800 °C for 1 h to get rid of binders. The conductivity of the samples was measured in the range 300 °C to 700 °C, with the exception of SrFe$_{0.6}$Ti$_{0.1}$O$_{3-δ}$ in 5% H$_2$/Ar which measured in the range 300 °C to 600 °C with a heating/cooling rate of 1 °C min$^{-1}$. Measurements in air and 5%H$_2$/Ar were conducted using an D.C. method by a pseudo-four-probe method using a Solartron 1287 electrochemical interface controlled by CorrWare software with a constant current of 0.01–0.1 A, as described in previous reports [24–26]. The temperature was digitally recorded in parallel with the impedance through an Omega HH506RA multi-logger thermometer connected to a
computer [26]. The conductivity in 5%H2/Ar was measured after reduction the samples in the same atmosphere at 700 °C for 10 h.

3. Results and discussion

3.1. XRD and STA of SrFe0.7TM0.2Ti0.1O3-δ (TM = Mn, Fe, Co, Ni, Cu)

X-ray diffraction of SrFe0.7Ti0.1O3-δ and SrFe0.7Mn0.2Ti0.1O3-δ (TM = Mn, Fe, Co, Ni, Cu) after synthesis in air exhibited perovskite structures, space group Pm-3m (No. 221), for all compounds as shown in Fig. 1, although with a small amount, 3.5% phase fraction, of an SrO impurity phase (PDF: 6-520) observed for sample SrFe0.7Ni0.2Ti0.1O3-δ. The representative GSAS plots for SrFe0.7Ti0.1O3-δ and SrFe0.7Mn0.2Ti0.1O3-δ with TM = Fe, Mn and Co are shown in Fig. 2. The refined lattice parameters are listed in Table 1. As shown in Fig. 3, a variation in the lattice parameters was exhibited which does not directly correlate with the variation in the average size of the dopant cations, with the lattice parameters reducing in the order Cu > Mn > Fe > Co > Ni. This is consistent to the trends of ionic radii for TM3+ ions at octahedral sites [27] although the real charge of TM ions in the SrFe0.7Ti0.1O3-δ series could be between TM2+ and TM3+.

In previous reports, all dopants exhibited a reduction of the average oxidation state of iron in SrFe0.7TiO3-δ with increasing dopant concentration, with the larger cation size of Fe3+ over Fe4+ and the reduction in oxygen content, would be observed with B2+ dopants. This is true for both cobalt and nickel, which, due to the dopant sizes correlating with the variation in the average size of the dopant cations, and the loss of oxygen from the structure, leading to lattice expansion. Doping of manganese elicits a minimal increase in the lattice parameter, 0.0019 Å, over SrFe0.7Mn0.2Ti0.1O3-δ which, due to the size of the Mn2+ cation (0.83 Å for Mn2+ oct = 0.66 Å for Mn2+ tet), is either suggestive of Mn3+ formation (0.645 Å for Mn1+ oct or 0.58 Å for Mn1+ tet) or of preferential tetrahedral coordination, balancing the reduction from the Fe3+-Fe4+ transition and the loss of oxygen from the structure. Further information on the oxidation state and coordination of the dopant cations or iron can only be obtained through additional analysis techniques, such as Mössbauer Spectroscopy or X-ray Photoelectron Spectroscopy (XPS).

Thermogravimetric analysis of SrFe0.7TM0.2Ti0.1O3-δ (TM = Mn, Fe, Co, Ni, Cu) in air are shown in Fig. 4a. The weight loss at low temperature is related to the loss of adsorbed water and gases and that at high temperature is related to loss of lattice oxygen. Samples SrFe0.7TM0.2Ti0.1O3-δ with TM = Fe, Co starts to lose oxygen at a temperature of ~450 °C whilst samples with TM = Mn, Cu starts to lose oxygen at ~500 °C indicating the latter is more stable in a reducing atmosphere. Sample SrFe0.7Ni0.2Ti0.1O3-δ kept losing weight during the whole process, possibly related to the presence of SrO impurity (Fig. 1). When stored at room temperature, the SrO may react with H2O to form Sr(OH)2 which will decompose on heating. Another possibility is that, sample SrFe0.7Ni0.2Ti0.1O3-δ, tends to lose weight at lower temperature indicating it is the least stable one in the investigated oxides. Differential scanning calorimetry, Fig. 4b, reveals a reversible thermal effects for all compounds, observed between 600 °C and 700 °C on heating and between 750 °C and 700 °C on cooling. This could be related to the loss of lattice oxygen on heating and gain oxygen on cooling [8]. Phase transition is unlikely because the oxides already exhibit a highly symmetric cubic structure whilst high temperature phase transition in perovskite is normally from low to high symmetry at evaluated temperatures [30, 31]. Further investigation is required.

### Table 1

<table>
<thead>
<tr>
<th>Material</th>
<th>SrFe0.7Mn0.2Ti0.1O3-δ</th>
<th>SrFe0.7Ti0.1O3-δ</th>
<th>SrFe0.7Co0.2Ti0.1O3-δ</th>
<th>SrFe0.7Ni0.2Ti0.1O3-δ</th>
<th>SrFe0.7Cu0.2Ti0.1O3-δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>X²</td>
<td>3.795</td>
<td>1.193</td>
<td>6.098</td>
<td>4.086</td>
<td>3.038</td>
</tr>
<tr>
<td>Rp (%)</td>
<td>6.40</td>
<td>5.21</td>
<td>7.15</td>
<td>9.75</td>
<td>5.64</td>
</tr>
<tr>
<td>wRp (%)</td>
<td>4.56</td>
<td>4.11</td>
<td>4.41</td>
<td>6.89</td>
<td>4.11</td>
</tr>
<tr>
<td>Space group</td>
<td>Pm-3m</td>
<td>Pm-3m</td>
<td>Pm-3m</td>
<td>Pm-3m</td>
<td>Pm-3m</td>
</tr>
<tr>
<td>a (Å)</td>
<td>3.8759(2)</td>
<td>3.8740(2)</td>
<td>3.8673(1)</td>
<td>3.8551(10)</td>
<td>3.8833(1)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>58.22(1)</td>
<td>58.14(1)</td>
<td>57.84(1)</td>
<td>57.29(4)</td>
<td>58.56(3)</td>
</tr>
<tr>
<td>Sr</td>
<td>x</td>
<td>x</td>
<td>y</td>
<td>z</td>
<td>Fe/TM/Ti</td>
</tr>
<tr>
<td>Uiso (Å)</td>
<td>0.009(7)</td>
<td>0.004(3)</td>
<td>0.007(1)</td>
<td>0.003(1)</td>
<td>0.012(1)</td>
</tr>
<tr>
<td>O</td>
<td>x</td>
<td>x</td>
<td>y</td>
<td>z</td>
<td>Fe/TM/Ti</td>
</tr>
<tr>
<td>Uiso (Å)</td>
<td>0.013(1)</td>
<td>0.006(6)</td>
<td>0.007(1)</td>
<td>0.001(1)</td>
<td>0.002(1)</td>
</tr>
</tbody>
</table>

The conductivities of SrFe0.7TM0.2Ti0.1O3-δ (TM = Mn, Fe, Co, Ni, Cu) in air are shown in Fig. 5. Compared to SrFe0.7O3-δ, the conductivities increase for all transition metal dopants, with all compounds. In the SrFe0.7Ti0.1O3-δ series, partially replacing iron by other transition elements Mn, Co, Ni and Cu leading to increased conductivity in air. It has been reported that the total electrical conductivity in SrFe1-xCo2xO3-δ increased when a large amount of cobalt was introduced in the solid solution [32]. Therefore it is also expected that sample SrFe0.7Co2xTi0.1O3-δ may exhibit high electrical conductivity than SrFe0.7Ti0.1O3-δ. As for elements Mn, Ni and Cu, they tend to exhibit lower state at high temperatures [33]. For charge balance, in samples co-doped with these elements, they can lose lattice oxygen to form more oxygen vacancies. This is likely to increase the oxygen ionic conductivity thus the total electrical conductivity increases as well. On the other hand, increase the charge of ion ions, say, more Fe3+ ions will exhibit the state of Fe4+ will lead to increased electronic conductivity [34]. The conductivity of SrFe0.7TM0.2Ti0.1O3-δ, SrFe0.7Co2xTi0.1O3-δ and SrFe0.7Cu2xTi0.1O3-δ remained between 5 S cm-1 and 20 S cm-1 over the measured temperature range, thus exhibiting potential for use as SOFC cathode materials. Previous research into La0.7Sr0.3CoO3-δ [35] suggests that the transition between semiconducting and metallic...
behaviour would still be observed for cobalt doped ferrites; however, the transition for La$_{0.8}$Sr$_{0.2}$Co$_{1-y}$Fe$_y$O$_{3-\delta}$ occurs as higher temperatures than the measurement temperature range used in this study. In our study, it is difficult to obtain pellets with higher relative density by conventional sintering method because the pellets melt at higher sintering temperature. The relatively low relative density may affect the measured conductivity because of the existence of void in the pellets. In general, the measured conductivity is lower than the specific conductivity (conductivity of a fully dense sample) [36–39]. In reported materials, difference between the measured apparent conductivity and specific conductivity is generally not big when the relative density is higher than 70% [37,39]. As the density of our samples is over 70%, the measured conductivity is lower than specific conductivity but should be fairly close.

3.3. STA and conductivity of SrFe$_0.7$TM$_0.2$Ti$_0.1$O$_{3-\delta}$ (TM = Mn, Fe, Co, Ni, Cu) in 5%H$_2$/Ar

Reduction of SrFe$_0.7$TM$_0.2$Ti$_0.1$O$_{3-\delta}$ (TM = Mn Ni, Cu) at 700 °C in 5% H$_2$/Ar exhibited a lower weight loss than was observed for SrFe$_0.9$Ti$_0.1$O$_{3-\delta}$ (Fig. 6). In contrast to the other doped compounds, SrFe$_0.7$Co$_0.2$Ti$_0.1$O$_{3-\delta}$ exhibited an increase in weight loss, 6.4%, compared to that for SrFe$_0.9$Ti$_0.1$O$_{3-\delta}$ 5.05%. The increased weight loss is likely indicative of reduction of cobalt at these temperatures. In general, in the presence of hydrogen, the oxides tend to lose weight at lower temperatures compared to those in air (Fig. 4).

The conductivities of the transition metal doped samples reduced at 700 °C in 5% H$_2$/Ar are shown in Fig. 7. The samples exhibited minor reductions in the conductivity, with the exception of the manganese.
The conductivity of the Mn doped sample demonstrated a reduction of several orders of magnitude, 14.69 S cm$^{-1}$ in air to 0.323 S cm$^{-1}$ in 5% H$_2$/Ar at 700 °C. This was also demonstrated in the increase in the activation energy upon reduction, from 0.226(1) eV to 0.516(1) eV. The semiconductor-metal transition observed in air is also exhibited, albeit at higher temperature, from 560 °C to 660 °C upon reduction, suggesting that the conduction mechanism does not change. The reduction in conductivity is likely associated with a significant decrease in the charge carrier concentration, as a result of cationic reduction. This may intimate that manganese dopes as Mn$^{3+}$, directly contributing to the charge carrier concentration in air, and not altering the charge carrier concentration through charge compensation mechanisms. Reduction of Mn$^{3+}$ to Mn$^{2+}$ upon exposure to 5% H$_2$/Ar would reduce the charge carrier concentration, similar to the Fe$^{4+}$-Fe$^{3+}$ transition. Significant reductions in the electronic conductivity is also observed for manganite perovskites, as a result of Mn$^{3+}$-Mn$^{2+}$ transitions [40]. It should be noted that the specific conductivities of the samples in a reducing atmosphere are expected higher than the measured apparent conductivity, as described above. Low relative density will not affect the application of these materials as electrode for solid oxide fuel cells or solid oxide electrolytic cells as the electrodes have to be porous to allow gas diffusion to the triple phase boundary to realize the electrochemical reactions on the electrodes [41–44].

3.4. XRD of reduced SrFe$_{0.7}$TM$_{0.2}$Ti$_{0.1}$O$_{3-δ}$ (TM = Mn, Fe, Co, Ni, Cu)

X-ray diffraction of SrFe$_{0.7}$TM$_{0.2}$Ti$_{0.1}$O$_{3-δ}$ (TM = Mn, Fe, Co, Ni, Cu) after reduction at 700 °C in 5% H$_2$/Ar are shown in Fig. 8. Little change in the material structure, with the exception of SrFe$_{0.7}$Ni$_{0.2}$Ti$_{0.1}$O$_{3-δ}$, is observed. This suggests that the conduction mechanism does not change. The reduction in conductivity is likely associated with a significant decrease in the charge carrier concentration, as a result of cationic reduction. This may intimate that manganese dopes as Mn$^{3+}$, directly contributing to the charge carrier concentration in air, and not altering the charge carrier concentration through charge compensation mechanisms. Reduction of Mn$^{3+}$ to Mn$^{2+}$ upon exposure to 5% H$_2$/Ar would reduce the charge carrier concentration, similar to the Fe$^{4+}$-Fe$^{3+}$ transition. Significant reductions in the electronic conductivity is also observed for manganite perovskites, as a result of Mn$^{3+}$-Mn$^{2+}$ transitions [40]. It should be noted that the specific conductivities of the samples in a reducing atmosphere are expected higher than the measured apparent conductivity, as described above. Low relative density will not affect the application of these materials as electrode for solid oxide fuel cells or solid oxide electrolytic cells as the electrodes have to be porous to allow gas diffusion to the triple phase boundary to realize the electrochemical reactions on the electrodes [41–44].

3.4. XRD of reduced SrFe$_{0.7}$TM$_{0.2}$Ti$_{0.1}$O$_{3-δ}$ (TM = Mn, Fe, Co, Ni, Cu)

X-ray diffraction of SrFe$_{0.7}$TM$_{0.2}$Ti$_{0.1}$O$_{3-δ}$ (TM = Mn, Fe, Co, Ni, Cu) after reduction at 700 °C in 5% H$_2$/Ar are shown in Fig. 8. Little change in the material structure, with the exception of SrFe$_{0.7}$Ni$_{0.2}$Ti$_{0.1}$O$_{3-δ}$, is observed. This suggests that the conduction mechanism does not change. The reduction in conductivity is likely associated with a significant decrease in the charge carrier concentration, as a result of cationic reduction. This may intimate that manganese dopes as Mn$^{3+}$, directly contributing to the charge carrier concentration in air, and not altering the charge carrier concentration through charge compensation mechanisms. Reduction of Mn$^{3+}$ to Mn$^{2+}$ upon exposure to 5% H$_2$/Ar would reduce the charge carrier concentration, similar to the Fe$^{4+}$-Fe$^{3+}$ transition. Significant reductions in the electronic conductivity is also observed for manganite perovskites, as a result of Mn$^{3+}$-Mn$^{2+}$ transitions [40]. It should be noted that the specific conductivities of the samples in a reducing atmosphere are expected higher than the measured apparent conductivity, as described above. Low relative density will not affect the application of these materials as electrode for solid oxide fuel cells or solid oxide electrolytic cells as the electrodes have to be porous to allow gas diffusion to the triple phase boundary to realize the electrochemical reactions on the electrodes [41–44].

3.4. XRD of reduced SrFe$_{0.7}$TM$_{0.2}$Ti$_{0.1}$O$_{3-δ}$ (TM = Mn, Fe, Co, Ni, Cu)

X-ray diffraction of SrFe$_{0.7}$TM$_{0.2}$Ti$_{0.1}$O$_{3-δ}$ (TM = Mn, Fe, Co, Ni, Cu) after reduction at 700 °C in 5% H$_2$/Ar are shown in Fig. 8. Little change in the material structure, with the exception of SrFe$_{0.7}$Ni$_{0.2}$Ti$_{0.1}$O$_{3-δ}$, is observed. This suggests that the conduction mechanism does not change. The reduction in conductivity is likely associated with a significant decrease in the charge carrier concentration, as a result of cationic reduction. This may intimate that manganese dopes as Mn$^{3+}$, directly contributing to the charge carrier concentration in air, and not altering the charge carrier concentration through charge compensation mechanisms. Reduction of Mn$^{3+}$ to Mn$^{2+}$ upon exposure to 5% H$_2$/Ar would reduce the charge carrier concentration, similar to the Fe$^{4+}$-Fe$^{3+}$ transition. Significant reductions in the electronic conductivity is also observed for manganite perovskites, as a result of Mn$^{3+}$-Mn$^{2+}$ transitions [40]. It should be noted that the specific conductivities of the samples in a reducing atmosphere are expected higher than the measured apparent conductivity, as described above. Low relative density will not affect the application of these materials as electrode for solid oxide fuel cells or solid oxide electrolytic cells as the electrodes have to be porous to allow gas diffusion to the triple phase boundary to realize the electrochemical reactions on the electrodes [41–44].

3.4. XRD of reduced SrFe$_{0.7}$TM$_{0.2}$Ti$_{0.1}$O$_{3-δ}$ (TM = Mn, Fe, Co, Ni, Cu)

X-ray diffraction of SrFe$_{0.7}$TM$_{0.2}$Ti$_{0.1}$O$_{3-δ}$ (TM = Mn, Fe, Co, Ni, Cu) after reduction at 700 °C in 5% H$_2$/Ar are shown in Fig. 8. Little change in the material structure, with the exception of SrFe$_{0.7}$Ni$_{0.2}$Ti$_{0.1}$O$_{3-δ}$, is observed. This suggests that the conduction mechanism does not change. The reduction in conductivity is likely associated with a significant decrease in the charge carrier concentration, as a result of cationic reduction. This may intimate that manganese dopes as Mn$^{3+}$, directly contributing to the charge carrier concentration in air, and not altering the charge carrier concentration through charge compensation mechanisms. Reduction of Mn$^{3+}$ to Mn$^{2+}$ upon exposure to 5% H$_2$/Ar would reduce the charge carrier concentration, similar to the Fe$^{4+}$-Fe$^{3+}$ transition. Significant reductions in the electronic conductivity is also observed for manganite perovskites, as a result of Mn$^{3+}$-Mn$^{2+}$ transitions [40]. It should be noted that the specific conductivities of the samples in a reducing atmosphere are expected higher than the measured apparent conductivity, as described above. Low relative density will not affect the application of these materials as electrode for solid oxide fuel cells or solid oxide electrolytic cells as the electrodes have to be porous to allow gas diffusion to the triple phase boundary to realize the electrochemical reactions on the electrodes [41–44].

3.4. XRD of reduced SrFe$_{0.7}$TM$_{0.2}$Ti$_{0.1}$O$_{3-δ}$ (TM = Mn, Fe, Co, Ni, Cu)

X-ray diffraction of SrFe$_{0.7}$TM$_{0.2}$Ti$_{0.1}$O$_{3-δ}$ (TM = Mn, Fe, Co, Ni, Cu) after reduction at 700 °C in 5% H$_2$/Ar are shown in Fig. 8. Little change in the material structure, with the exception of SrFe$_{0.7}$Ni$_{0.2}$Ti$_{0.1}$O$_{3-δ}$, is observed. This suggests that the conduction mechanism does not change. The reduction in conductivity is likely associated with a significant decrease in the charge carrier concentration, as a result of cationic reduction. This may intimate that manganese dopes as Mn$^{3+}$, directly contributing to the charge carrier concentration in air, and not altering the charge carrier concentration through charge compensation mechanisms. Reduction of Mn$^{3+}$ to Mn$^{2+}$ upon exposure to 5% H$_2$/Ar would reduce the charge carrier concentration, similar to the Fe$^{4+}$-Fe$^{3+}$ transition. Significant reductions in the electronic conductivity is also observed for manganite perovskites, as a result of Mn$^{3+}$-Mn$^{2+}$ transitions [40]. It should be noted that the specific conductivities of the samples in a reducing atmosphere are expected higher than the measured apparent conductivity, as described above. Low relative density will not affect the application of these materials as electrode for solid oxide fuel cells or solid oxide electrolytic cells as the electrodes have to be porous to allow gas diffusion to the triple phase boundary to realize the electrochemical reactions on the electrodes [41–44].

3.4. XRD of reduced SrFe$_{0.7}$TM$_{0.2}$Ti$_{0.1}$O$_{3-δ}$ (TM = Mn, Fe, Co, Ni, Cu)

X-ray diffraction of SrFe$_{0.7}$TM$_{0.2}$Ti$_{0.1}$O$_{3-δ}$ (TM = Mn, Fe, Co, Ni, Cu) after reduction at 700 °C in 5% H$_2$/Ar are shown in Fig. 8. Little change in the material structure, with the exception of SrFe$_{0.7}$Ni$_{0.2}$Ti$_{0.1}$O$_{3-δ}$, is observed. This suggests that the conduction mechanism does not change. The reduction in conductivity is likely associated with a significant decrease in the charge carrier concentration, as a result of cationic reduction. This may intimate that manganese dopes as Mn$^{3+}$, directly contributing to the charge carrier concentration in air, and not altering the charge carrier concentration through charge compensation mechanisms. Reduction of Mn$^{3+}$ to Mn$^{2+}$ upon exposure to 5% H$_2$/Ar would reduce the charge carrier concentration, similar to the Fe$^{4+}$-Fe$^{3+}$ transition. Significant reductions in the electronic conductivity is also observed for manganite perovskites, as a result of Mn$^{3+}$-Mn$^{2+}$ transitions [40]. It should be noted that the specific conductivities of the samples in a reducing atmosphere are expected higher than the measured apparent conductivity, as described above. Low relative density will not affect the application of these materials as electrode for solid oxide fuel cells or solid oxide electrolytic cells as the electrodes have to be porous to allow gas diffusion to the triple phase boundary to realize the electrochemical reactions on the electrodes [41–44].
which exhibits a 5.6% phase fraction of NiO (PDF: 4-835) and a 4.4% phase fraction of Ni (PDF: 6-696) and SrFe0.9Ti0.1O3-δ which exhibits an unidentified impurity phase. A small amount of Co3O4 (PDF: 80-1545) was also observed. SrFe0.7Co0.2Ti0.1O3-δ and SrFe0.7Mn0.2Ti0.1O3-δ upon reduction. The redox instability observed for the nickel and cobalt doped phase is likely due to the reducibility of the nickel and cobalt within the structure, further implied by exfoliation of nickel metal. This has also been observed for other nickel or cobalt doped perovskite materials [47-49].

GSAS [23] analysis of these compounds exhibits an increase in the lattice parameters for SrFe0.7Co0.2Ti0.1O3-δ, SrFe0.7Co0.2Ti0.1O3-δ, and SrFe0.7Co0.2Ti0.1O3-δ. The cubic perovskite structure was observed for all dopants for SrFe0.7TM0.2Ti0.1O3-δ (TM = Mn, Fe, Co, Ni, Cu), with variation in the lattice parameters associated with different dopant environments and charge compensation mechanisms. Improvement of the electronic conductivity over SrFe0.7Ti0.1O3-δ was observed for all dopants in air, attributed to increasing charge carrier concentration. Reduction in 5% H2/Ar exhibited minimal variation in material properties SrFe0.7Cu0.2Ti0.1O3-δ, with a significant reduction in conductivity was observed for SrFe0.7Mn0.2Ti0.1O3-δ. A small amount of SrO was observed in sample with nominal composition SrFe0.7Cu0.2Ti0.1O3-δ. All doped compounds exhibited a single phase cubic perovskite structure after reduction with the exception of SrFe0.7Co0.2Ti0.1O3-δ and SrFe0.7Co0.2Ti0.1O3-δ, which display secondary nickel and cobalt phases respectively upon reduction.

4. Conclusions

The cubic perovskite structure was observed for all dopants for SrFe0.7TM0.2Ti0.1O3-δ (TM = Mn, Fe, Co, Ni, Cu), with variation in the lattice parameters associated with different dopant environments and charge compensation mechanisms. Improvement of the electronic conductivity over SrFe0.7Ti0.1O3-δ was observed for all dopants in air, attributed to increasing charge carrier concentration. Reduction in 5% H2/Ar exhibited minimal variation in material properties SrFe0.7Cu0.2Ti0.1O3-δ, with a significant reduction in conductivity was observed for SrFe0.7Mn0.2Ti0.1O3-δ. A small amount of SrO was observed in sample with nominal composition SrFe0.7Cu0.2Ti0.1O3-δ. All doped compounds exhibited a single phase cubic perovskite structure after reduction with the exception of SrFe0.7Co0.2Ti0.1O3-δ and SrFe0.7Co0.2Ti0.1O3-δ, which display secondary nickel and cobalt phases respectively upon reduction.

The significant improvement in the conductivity and stability upon doping of SrFe0.7Ti0.1O3-δ suggests that a more suitable parent compound may produce further improvements in material conductivity and stability. SrFe0.7Cu0.2Ti0.1O3-δ are redox stable at a temperature below 700 °C and highly conductive with conductivities around 10 S cm−1 in both air and reducing atmosphere which are about five times higher than those of pure SrFe0.9Ti0.1O3-δ. In the investigated oxides, in terms of conductivity and redox stability, SrFe0.7Cu0.2Ti0.1O3-δ exhibits promising properties for use as a potential electrode material for symmetrical/reversible SOFCs.

Acknowledgements

The authors thank EPSRC Flame SOFCs (EP/K021036/2), UK-India Biogas SOFCs (EP/I037016/1) and SuperGen Fuel Cells (EP/G030995/1).
projects for funding. We also thank Natural Science Foundation of China (NSFC21628301) for support. One of the authors (Cowin) thanks ScotChem SPIRIT scheme for support of his PhD study.

References