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DOI:
10.3390/cryst7060169

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Document Version
Publisher's PDF, also known as Version of record

Citation for published version (Harvard):
Jarvis, A & Slater, P 2017, 'Investigation into the Effect of Sulfate and Borate Incorporation on the Structure and Properties of SrFeO3-', Crystals, vol. 7, no. 6. https://doi.org/10.3390/cryst7060169

Link to publication on Research at Birmingham portal

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Investigation into the Effect of Sulfate and Borate Incorporation on the Structure and Properties of SrFeO$_{3-\delta}$

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Abstract: In this paper, we demonstrate the successful incorporation of sulfate and borate into SrFeO$_{3-\delta}$, and characterise the effect on the structure and conductivity, with a view to possible utilisation as a cathode material in Solid Oxide Fuel Cells. The incorporation of low levels of sulfate/borate is sufficient to cause a change from a tetragonal to a cubic cell. Moreover, whereas heat treatment of undoped SrFeO$_{3-\delta}$ under N$_2$ leads to a transformation to brownmillerite Sr$_2$Fe$_2$O$_5$ with oxygen vacancy ordering, the sulfate/borate-doped samples remain cubic under the same conditions. Thus, sulfate/borate doping appears to be successful in introducing oxide ion vacancy disorder in this system.

Keywords: solid oxide fuel cell; cathode; perovskite; sulfate; borate

1. Introduction

Research into solid oxide fuel cells (SOFCs) as alternate energy materials has grown due to their high efficiency and consequent reduction in greenhouse gas emissions. Specifically, research into perovskite materials has attracted significant interest for potential SOFC materials including cathode, electrolyte and anode materials (see, for example, the review articles [1,2]). Traditionally, doping strategies for perovskite materials has involved the introduction of cations of a similar size e.g., Sr$^{2+}$ for La$^{3+}$, Mg$^{2+}$ for Ga$^{3+}$ to give the oxide ion conducting electrolyte La$_{1-x}$Sr$_x$Ga$_{1-y}$Mg$_y$O$_{3-\frac{x}{2}-\frac{y}{2}}$ [3]. More recently, we have applied oxyanion (silicate, phosphate, sulfate, borate) doping strategies to improve the properties of solid oxide fuel cell materials, initially demonstrating the successful incorporation into Ba$_2$In$_2$O$_5$ [4]. Research on oxyanion incorporation into perovskites was initially reported for superconducting cuprate materials. This work showed that a wide range of oxyanions (carbonate, borate, nitrate, sulfate, and phosphate) could be incorporated into the perovskite structure [5–12]. In this doping strategy, the central ion of the oxyanion group is located on the perovskite B cation site, with the oxygens of this group occupying either three (borate, carbonate, nitrate) or four (sulfate, phosphate) of the available six anion positions around this site, albeit suitably displaced to achieve the correct coordination for the oxyanion group. As an extension to this work on cuprate superconductors, we have demonstrated successful oxyanion doping of perovskite materials for SOFC applications. This has included oxyanion (sulfate, silicate, phosphate) doping of Ba$_2$(In/Sc)$_2$O$_5$ electrolyte materials [13–16]. Doping with these oxyanions introduces disorder on the oxygen sublattice, leading to improvements in the ionic conductivity. This work has also been extended to potential solid oxide fuel cell electrode materials, with successful oxyanion doping in the perovskite systems SrCoO$_3$ [17–20], SrCo$_{0.85}$Fe$_{0.15}$O$_3$ [21], SrMnO$_3$ [18], CaMnO$_3$ [22] and SrFeO$_{3-\delta}$ [23], with the results suggesting improved performance/stability.
Following the prior work demonstrating the successful incorporation of silicate into SrFeO$_3$-$\delta$ [23], we report in this paper an investigation into the effect of sulfate and borate doping. The undoped system SrFeO$_3$-$\delta$ has attracted interest due to its high ionic and electronic conductivity, however under low p(O$_2$) the oxide ion (and electronic conductivity) are significantly reduced. This is due to oxygen loss leading to a transformation to the oxygen vacancy ordered brownmillerite structure, Sr$_2$Fe$_2$O$_5$ (Figure 1). We have therefore investigated the effect of borate/sulfate doping on this transformation.

2. Results and Discussion

2.1. SrFe$_{1-x}$S$_x$O$_{3-\delta}$

2.1.1. X-ray Diffraction Data

A range of samples of SrFe$_{1-x}$S$_x$O$_{3-\delta}$ with increasing sulfate content (0 $\leq$ x $\leq$ 0.1) were prepared. X-ray diffraction analysis showed that without sulfate doping SrFeO$_3$-$\delta$ forms a tetragonal perovskite in line with prior reports. This is illustrated in Figure 2 (expanded region 2$\theta$ = 45° to 60°) where peak splitting can clearly be observed. Upon doping with sulfate, there is a transformation to a cubic cell (0.025 $\leq$ x $\leq$ 0.075), where no peak splitting is now observed (Figure 2). Above x $= 0.075$, small SrSO$_4$ impurities appear, suggesting that the solubility limit of sulfate in SrFe$_{1-x}$S$_x$O$_{3-\delta}$ is x $\approx$ 0.075.

![Figure 1. Structure of Sr$_2$Fe$_2$O$_5$ (showing oxygen vacancy ordering) (left) and SrFeO$_3$ (right).](image1)

![Figure 2. Cont.](image2)
were prepared without addition of sulfate. The X-ray diffraction data for SrFe 0.95O3-
parent phase. In contrast, impurities are not observed for the sulfate-containing phase SrFe 0.95S0.05O3-

The variation of the cell parameters for SrFe 0.95O3-δ and this will be discussed in more detail in Section 2.1.4. The data show a small general increase with increasing sulfate content, and this will be discussed in more detail in Section 2.1.4.

In order to provide further support for the incorporation of sulfate, equivalent Fe-deficient samples were prepared without addition of sulfate. The X-ray diffraction data for SrFe 0.95O3-δ (Fe-deficient, no sulfate) and SrFe 0.95S0.05O3-δ are compared in Figure 3. These data show the presence of impurities for SrFe 0.95O3-δ along with peak splitting, consistent with a tetragonal cell, as for the undoped SrFeO3-δ parent phase. In contrast, impurities are not observed for the sulfate-containing phase SrFe 0.95S0.05O3-δ, and the cell is now cubic. Therefore, this comparison provides further evidence for the successful incorporation of sulfate.

Cell parameters for all these phases were determined using the Rietveld method (an example fit is shown in Figure 4). The variation of the cell parameters for SrFe 1-xSxO3-δ with increasing sulfate content is given in Table 1. The data show a small general increase with increasing sulfate content, and this will be discussed in more detail in Section 2.1.4.
In addition to the determination of the unit cell parameters, site occupancies were refined for the Fe/S site. These occupancies are given in Table 1, and show that the refined values are in good agreement with the expected values.

Table 1. Lattice parameters and Fe/S site occupancies obtained from Rietveld refinement using XRD data for SrFe$_{1-x}$S$_x$O$_{3-\delta}$. The structure of SrFeO$_{3-\delta}$ was refined using a tetragonal space group (P4/mmm). The structures of the sulfate-doped samples were refined using a cubic space group (Pm$3\bar{m}$).

| SrFe$_{1-x}$S$_x$O$_{3-\delta}$ | S (x) 0 0.025 0.05 0.075 | a (Å) 3.8648(1) 3.8723(1) 3.8776(1) 3.8766(1) |
|-------------------------------|--------------------------|---------------------------------------------|
|                               | c (Å) 3.8487(1) - - - -   | V ($\text{Å}^3$) 57.486(4) 58.066(2) 58.303(4) 58.260(4) |
|                               | R$_{wp}$ (%) 1.84 1.67 2.01 1.97 | R$_{exp}$ (%) 0.92 0.92 0.90 0.90 |
|                               | Fe occupancy 1 0.98(1) 0.96(1) 0.94(1) | S occupancy - 0.02(1) 0.04(1) 0.06(1) |
|                               | Fe/S Uiso 0.003(1) 0.009(1) 0.011(1) 0.008(1) | |

2.1.2. Stability under N$_2$

The effect of heating the SrFe$_{1-x}$S$_x$O$_{3-\delta}$ samples under N$_2$ was then examined. Upon heating under N$_2$ to 950 °C, the X-ray diffraction data showed that SrFeO$_{3-\delta}$ transforms to the oxygen vacancy ordered brownmillerite type Sr$_2$Fe$_2$O$_5$ (Figures 1 and 5). This would be expected to be unfavorable for fuel cell applications due to the ordering of oxygen vacancies, which is expected to lower the oxide ion conductivity. In contrast, for the sulfate-doped samples, the disordered cubic perovskite is retained under a similar heat treatment. For the x = 0.025 sample, there are some very weak peaks (see expanded XRD figure) associated with the brownmillerite structure, but for the higher sulfate contents (x $\geq$ 0.05), a single phase cubic cell is observed. In line with the reduction in the Fe oxidation state towards 3+, there is an increase in the cell parameters associated with the larger size of Fe$^{3+}$ versus Fe$^{4+}$ (Table 2).
Figure 5. X-ray diffraction patterns of (a) SrFeO$_{3-\delta}$, (b) SrFe$_{0.975}$S$_{0.025}$O$_{3-\delta}$, and (c) SrFe$_{0.95}$S$_{0.05}$O$_{3-\delta}$ after heating under N$_2$ to 950 °C.

| SrFe$_{1-x}$S$_x$O$_{3-\delta}$ |       |       |
|------------------------------|-------|-------|
| $S(x)$ | 0.025 | 0.05  | 0.075 |
| a (Å)  |       |       |       |
| 3.8723(1) | 3.9231(1) | 3.8776(1) | 3.9256(1) | 3.8766(1) | 3.9280(1) |
| c (Å)  |       |       |       |
| -      |       |       |       |       |       |
| V (Å$^3$) |       |       |       |
| 58.066(2) | 60.379(1) | 58.303(4) | 60.496(1) | 58.260(4) | 60.606(1) |
| R$_{wp}$ (%) |       |       |       |
| 1.67 | 3.10 | 2.01 | 3.09 | 1.97 | 3.20 |
| R$_{exp}$ (%) |       |       |       |
| 0.92 | 2.59 | 0.90 | 2.51 | 0.90 | 2.50 |

2.1.3. Thermogravimetric Analysis

Thermogravimetric analysis (TGA) (heat treatment in N$_2$ to reduce the Fe oxidation state to 3+) was then utilized to determine the oxygen contents of the samples as prepared in air. This analysis resulted in an interesting observation associated with Mass spectrometry analysis of the evolved gas. For the undoped sample SrFeO$_{3-\delta}$, the loss of mass is only associated with oxygen as indicated by the mass spectrometry data. However, for the sulfate-doped samples, a mass loss associated with CO$_2$ was observed in addition to the expected mass loss due to O$_2$.

Thus, the results indicated the presence of some carbonate in the sulfate-doped samples. In order to remove this carbonate, heat treatment in O$_2$ (up to 900 °C) was carried out for these SrFe$_{1-x}$S$_x$O$_{3-\delta}$ samples. After this oxygen treatment, TGA analysis indicated no presence of carbonate. This is illustrated in Figure 6, where a mass loss associated with CO$_2$ is not observed after heat treatment in O$_2$ for SrFe$_{0.95}$S$_{0.05}$O$_{3-\delta}$. 

The TGA results indicating the presence of carbonate may at first glance suggest the existence of a small amount of SrCO₃ impurity. However, the temperature at which the CO₂ is lost is significantly lower than would be expected for SrCO₃. In order to illustrate this, TGA data for SrCO₃ were also collected and compared to the data for the SrFe₀.₉₅S₀.₀₅O₃₋δ. This experiment shows a significant difference in the temperature at which the loss of CO₂ occurs for SrFe₀.₉₅S₀.₀₅O₃₋δ and SrCO₃. In particular, the starting temperature for CO₂ loss for SrFe₀.₉₅S₀.₀₅O₃₋δ occurs at a significantly lower temperature (≈490 °C vs. ≈760 °C for SrCO₃), which may suggest that this carbonate is present in the perovskite structure, i.e., we have a mixed sulfate/carbonate-doped sample—SrFe₁₋ₓSₓCₓO₃₋δ. Further work is required to investigate this possibility, although as noted in the introduction, carbonate has been shown previously to be accommodated in perovskite materials.

Given the dual (O₂ and CO₂) mass loss for the air-synthesized SrFe₁₋ₓSₓO₃₋δ samples, it is not possible to determine reliable oxygen contents for these samples. In addition, as detailed by Starkov et al., the determination of oxygen contents in partially substituted ferrites is non-trivial without a reliable fixed reference point [24]. Since it is possible that there may still be a small amount of Fe⁴⁺ in these samples after the N₂ treatment, there is not a conclusive fixed reference oxygen point, and so any calculated oxygen contents would only be rough approximations.

2.1.4. Heat Treatment under O₂

The samples (described above) heated under O₂ were also examined by X-ray diffraction (Figure 7). All the sulfate-doped SrFe₁₋ₓSₓO₃₋δ samples were shown to retain their original cubic structure while undoped SrFeO₃₋δ remained tetragonal.
Lattice parameters and Fe/S site occupancies for SrFe$_{1-x}$S$_x$O$_{3-\delta}$, obtained from Rietveld refinement using XRD data for SrFe$_{1-x}$S$_x$O$_{3-\delta}$ after heating in O$_2$.

|                | SrFe$_{1-x}$S$_x$O$_{3-\delta}$ Heated in O$_2$ |
|----------------|-----------------------------------------------|
| S (x)          | 0                                            |
| a (Å)          | 3.8651(1)                                    |
| c (Å)          | 3.8477(1)                                    |
| V (Å$^3$)      | 57.349(3)                                    |
| $R_{wp}$ (%)   | 4.16                                         |
| $R_{exp}$ (%)  | 3.71                                         |
| Fe occ         | 1(-)                                         |
| S occ          | -                                            |
|                | 0.025                                        |
|                | 0.05                                         |
|                | 0.075                                        |

Table 3
Figure 8. Plot of unit cell volume vs. x for SrFe$_{1-x}$S$_x$O$_{3-\delta}$ heated in air (●) and heated in O$_2$ (■).

2.1.5. Conductivity Data

Following the successful incorporation of sulfate, the conductivities of the SrFe$_{1-x}$S$_x$O$_{3-\delta}$ samples were examined in air. In general, the SrFe$_{1-x}$S$_x$O$_{3-\delta}$ samples were found to have similar conductivities, with the exception of a notable decrease at lower temperatures for the higher sulfate content (x = 0.075) sample (Figure 9). This observation of a decrease in conductivity for higher dopant levels is comparable to the silicon-doped SrFeO$_{3-\delta}$ system where it was proposed that at higher doping levels the silicate disrupts the Fe-O network resulting in a decrease in conductivity. [23]. Another factor, however, could relate to low levels of insulating impurities in this high sulfate content sample, given that the cell parameter data suggest that the sulfate solubility limit may be closer to x = 0.05.

Figure 9. Plot of log $\sigma$ vs. 1000/T for SrFeO$_{3-\delta}$ (●), SrFe$_{0.95}$S$_{0.05}$O$_{3-\delta}$ (○), SrFe$_{0.95}$S$_{0.05}$O$_{3-\delta}$ (■) and SrFe$_{0.925}$S$_{0.075}$O$_{3-\delta}$ (□) in air.

2.2. SrFe$_{1-x}$B$_x$O$_{3-\delta}$

2.2.1. X-ray Diffraction Data

The possible incorporation of borate into SrFeO$_{3-\delta}$ was then examined, with samples of SrFe$_{1-x}$B$_x$O$_{3-\delta}$ prepared for 0 ≤ x ≤ 0.15. The results showed that a higher borate content was achievable compared to the sulfate-doped samples, with single phase borate-doped samples for x ≤ 0.1.
In terms of the effect of borate incorporation on the structure, similar results were observed as for the SrFe$_{1-x}$S$_x$O$_{3-\delta}$ samples. In particular, borate doping resulted in a similar cubic cell as for the sulfate-doped samples.

Cell parameters and site occupancies were determined using the Rietveld method (an example fit is shown in Figure 11).

The refinements gave Fe/B occupancies in good agreement with those expected (Table 4). Furthermore, in this case, a decrease in the unit cell was observed on borate doping in agreement with the smaller size of B$^{3+}$ compared to Fe$^{3+/4+}$, and the fact that unlike the situation for sulfate doping there is no additional oxygen associated with the dopant (i.e., we are effectively replacing Fe(III)O$_{1.5}$ with BO$_{1.5}$).
Table 4. Lattice parameters and Fe/B site occupancies obtained from Rietveld analysis using X-ray diffraction data for SrFe$_{1-x}$B$_x$O$_{3-\delta}$. The structure of SrFeO$_{3-\delta}$ was refined using a tetragonal space group (P4/mmm). The structures of the doped samples were refined using a cubic space group (Pm3m).

| SrFe$_{1-x}$B$_x$O$_{3-\delta}$ | 0   | 0.05 | 0.1 |
|-------------------------------|-----|------|-----|
| B (x)                         | 0   | 0.05 | 0.1 |
| a (Å)                         | 3.8648(1) | 3.8593(1) | 3.8561(1) |
| c (Å)                         | 3.8487(1) | -    | -   |
| V (Å$^3$)                     | 57.486(4) | 57.483(2) | 57.336(4) |
| Rwp (%)                       | 1.84 | 3.23 | 3.67 |
| Rexp (%)                      | 0.92 | 2.30 | 2.52 |
| Fe occupancy                  | 1   | 0.92(1) | 0.89(1) |
| B occupancy                   | -   | 0.08(1) | 0.11(1) |
| Fe/B Uiso                     | 0.003(1) | 0.015(1) | 0.022(1) |

2.2.2. Stability under N$_2$

Heat treatment of the SrFe$_{1-x}$B$_x$O$_{3-\delta}$ samples at 950 °C under N$_2$ showed similar results to those observed on sulfate doping, with the borate-containing samples remaining cubic after this heat treatment in nitrogen (Figure 12). In line with the reduction of the Fe oxidation state to Fe$^{3+}$, there was a shift in the peak positions to lower angles, indicating a larger unit cell.

![X-ray diffraction patterns](image)

**Figure 12.** X-ray diffraction patterns for (a) SrFe$_{0.95}$B$_{0.05}$O$_{3-\delta}$, (b) SrFe$_{0.95}$B$_{0.05}$O$_{3-\delta}$ after heating under N$_2$, (c) SrFe$_{0.9}$B$_{0.1}$O$_{3-\delta}$, (d) SrFe$_{0.9}$B$_{0.1}$O$_{3-\delta}$ after heating under N$_2$.

2.2.3. Thermogravimetric Analysis

These samples were then analysed by TGA (heat treatment under N$_2$). In contrast to the air synthesised SrFe$_{1-x}$S$_x$O$_{3-\delta}$ samples, there was no mass loss due to CO$_2$ observed in these SrFe$_{1-x}$B$_x$O$_{3-\delta}$ systems, thus indicating no carbonate present.

2.2.4. Conductivity Data

For the SrFe$_{1-x}$B$_x$O$_{3-\delta}$ samples (x = 0.05, 0.1), the conductivity data showed significantly lower conductivities at lower temperatures compared with the undoped system (Figure 13). However, above 600 °C, the conductivities were comparable with the x = 0.1 sample, in particular showing a small improvement in the conductivity compared with undoped SrFeO$_{3-\delta}$. Notably, these temperatures are in the range where operation as a cathode in a solid oxide fuel cell would be.
Conductivity values (at 700 °C) for the borate- and sulfate-doped samples are shown in Table 5, and compared to the equivalent data for silicate-doped SrFeO$_3$-$\delta$ (from reference [23]). The data show similar values for all samples at this typical solid oxide fuel cell operating temperature.

Table 5. Conductivity data in air at 700 °C for SrFe$_{1-x}$M$_x$O$_3$-$\delta$ where M = Si [23], S and B.

| Si (x) | S (x) | B (x) |
|--------|-------|-------|
| 0 | 0.05 | 0.1 |
| 0.15 | 18 | 26 |
| 0 | 0.025 | 0.05 |
| 0.075 | 25 | 30 |
| 0.05 | 25 | 30 |
| 0.1 | 32 |

3. Experimental

High-purity SrCO$_3$, Fe$_2$O$_3$, (NH$_4$)$_2$SO$_4$, and H$_3$BO$_3$ were used to prepare SrFe$_{1-x}$S$_x$/B$_x$O$_3$-$\delta$ samples. Stoichiometric mixtures of the powders were intimately ground and initially heated to 900 °C (4 °C/min) for 12 h. Samples were then ballmilled (350 rpm for 1 h, Fritsch Pulverisette 7 planetary Mill) and reheated to 1000, 1050 and 1100 °C for 12 h with ballmilling of samples between heat treatments. For the SrFe$_{1-x}$B$_x$O$_3$-$\delta$ (x = 0.05, 0.1) samples, a higher temperature (1200 °C) heat treatment was required to achieve single phase samples. In order to ensure maximum oxygen content, all samples underwent a final heat treatment at 350 °C for 12 h in air.

Additionally, portions of the SrFe$_{1-x}$S$_x$O$_3$-$\delta$ (x = 0, 0.025, 0.05, 0.075) samples were heated to 900 °C under oxygen for 12 h with slow cooling at 50 °C/h to 350 °C, with the samples then maintained at this temperature for 12 h followed by cooling at 50 °C/h to room temperature. To test the stability under low p(O$_2$) conditions, both sulfate and borate-doped samples were heated under N$_2$ to 950 °C for 12 h.

Powder X-ray diffraction data were used in order to determine lattice parameters and phase purity. For SrFe$_{1-x}$S$_x$O$_3$-$\delta$ samples heated in air, X-ray diffraction data were collected on a Panalytical Empyrean diffractometer equipped with a Pixelc 2D detector (Cu Ka radiation). For the remaining SrFe$_{1-x}$S$_x$O$_3$-$\delta$ and SrFe$_{1-x}$B$_x$O$_3$-$\delta$ samples, a Bruker D8 diffractometer with Cu Kα$_1$ radiation was used.

![Figure 13. Plot of log σ vs. 1000/T for SrFeO$_3$-$\delta$ (●), SrFe$_{0.95}$B$_{0.05}$O$_3$-$\delta$ (○), SrFe$_{0.9}$B$_{0.1}$O$_3$-$\delta$ (■) in air.](image-url)
Samples were also analysed using thermogravimetric analysis (Netzsch STA 449 F1 Jupiter Thermal Analyser with mass spectrometry attachment). Samples were heated to 950 °C in N₂ (10 °C/min) and held for 30 min to reduce the iron oxidation state to Fe³⁺.

Pellets for conductivity measurements were prepared as follows: powders of SrFe₁₋ₓSₓO₃₋δ and SrFe₁₋ₓBₓO₃₋δ heated in air were initially ball milled (350 rpm for 1 h), before pressing into compacts and sintering at 1100 °C (SrFe₁₋ₓSₓO₃₋δ) and 1200 °C (SrFe₁₋ₓBₓO₃₋δ) for 12 h in air. Four Pt electrodes were attached with Pt paste and the samples were heated at 900 °C for 1 h in air. Samples were then furnace cooled to 350 °C and held at this temperature for 12 h to ensure full oxygenation. Conductivities were measured using the four probe dc method.

4. Conclusions

The results presented in this paper demonstrate the first reports of successful incorporation of sulfate and borate into SrFeO₃₋δ. This doping strategy results in a change from a tetragonal to a cubic cell, which is maintained even after heating under N₂, where undoped SrFeO₃₋δ transforms to the oxygen vacancy ordered brownmillerite structure. Conductivity data in air show that the borate/sulfate-doped samples have comparable conductivities (Table 5) to undoped SrFeO₃₋δ at solid oxide fuel cell operating temperatures. Given these initial promising results, further studies are warranted to investigate the performance of these doped systems as solid oxide fuel cell cathodes.

Acknowledgments: We would like to thank EPSRC for funding (studentship for Abbey Jarvis). The raw datasets associated with the results shown in this paper are available from the University of Birmingham archive: http://epapers.bham.ac.uk/3011/.

Author Contributions: P.R.S. conceived and designed the experiments; A.J. performed the experiments; A.J. and P.R.S. analysed the data; A.J. and P.R.S. wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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