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Antisite-disorder, magnetic and thermoelectric properties of Mo-rich Sr$_2$Fe$_{1-y}$Mo$_{1+y}$O$_6$ (0 ≤ y ≤ 0.2) double perovskites

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Structure analysis using X-ray and neutron powder diffraction and elemental mapping has been used to demonstrate that nominal A-site deficient Sr$_{2-x}$FeMoO$_{6-\delta}$ (0 ≤ x ≤ 0.5) compositions form as Mo-rich Sr$_2$Fe$_{1-y}$Mo$_{1+y}$O$_6$ (0 ≤ y ≤ 0.2) double perovskites at high temperatures and under reducing atmospheres. These materials show a gradual transition from the Fe and Mo rock salt ordered double perovskite structure to a B-site disordered arrangement. Analysis of the fractions of B-O-B' linkages revealed a gradual increase in the number of Mo-O-Mo linkages at the expense of the ferrimagnetic (FIM) Fe-O-Mo linkages that dominate the y = 0 material. All samples contain about 10-15% antiferromagnetic (AF) Fe-O-Fe linkages, independent of the degree of B-site ordering. The magnetic susceptibility of the y = 0.2 sample is characteristic of a small domain ferrimagnet ($T_c$ ~ 250 K), while room temperature neutron powder diffraction demonstrated the presence of G-type AF ordering linked to the Fe-O-Fe linkages ($m_{Fe} = 1.25(7) \mu_B$). The high temperature thermoelectric properties are characteristic of a metal with a linear temperature dependence of the Seebeck coefficient, S (for all y) and electrical resistivity $\rho$ (y ≥ 0.1). The largest thermoelectric power factor $S^2/\rho = 0.12$ mW m$^{-1}$ K$^{-1}$ is observed for Sr$_2$FeMoO$_6$ at 1000 K.
Introduction

Thermoelectric modules are widely considered as an important component for a sustainable energy future.\textsuperscript{1, 2} Traditionally these devices use p- and n-type semiconductors such as Bi\textsubscript{2}Te\textsubscript{3}, PbTe and Si\textsubscript{1-x}Ge\textsubscript{x} to convert heat into electricity. The efficiency of a thermoelectric material is given by its figure of merit: $ZT = (S^2/\rho\kappa)T$, where $S$ is the Seebeck coefficient, $\rho$ is the electrical resistivity, $\kappa$ ($\kappa_{el} + \kappa_{lat}$) is the thermal conductivity (sum of the electronic and lattice thermal conductivities) and $T$ is the absolute temperature. For good thermoelectric performance, materials with a large power factors ($S^2\sigma$) and low $\kappa$ are needed. Transition metal oxides have only relatively recently been appreciated as promising thermoelectric materials. Their advantageous properties include high-temperature stability, non-toxicity, in many cases low cost, and compatibility with CMOS fabrication techniques.\textsuperscript{3, 4} The main disadvantage is that most oxides have poor power factors. This perception changed after the discovery of high $S^2\sigma$ in metallic p-type Na\textsubscript{x}CoO\textsubscript{2}.\textsuperscript{5} Thereafter, several other oxide based materials have been explored such as ZnO,\textsuperscript{6, 7} SrTiO\textsubscript{3},\textsuperscript{8, 9} (misfit) cobaltates,\textsuperscript{10-13} and CaMnO\textsubscript{3}.\textsuperscript{14, 15} Despite this considerable research effort, the performance of most of the oxides investigated remains poor compared to the traditional semiconductor materials, and the search for novel efficient oxide materials is ongoing.

The double perovskite Sr\textsubscript{2}FeMoO\textsubscript{6} ($A_2BB’O_6$) has been extensively investigated due to its large low field magnetoresistances and spin-polarised conduction.\textsuperscript{16} The polarised conduction arises from a double exchange type mechanism where itinerant down-spin Mo\textsuperscript{5+} ($t_{2g}^{1}; S = 1/2$) electrons align non-conducting up-spin Fe\textsuperscript{3+} ($t_{2g}^{3}e_g^{2}; S = 5/2$) electrons, resulting in a FIM spin structure with a magnetisation of $2(5/2-1/2) = 4 \mu_B$ per formula unit.\textsuperscript{16, 17} From a chemical perspective, Sr\textsubscript{2}FeMoO\textsubscript{6} can be considered to be in a Fe\textsuperscript{2+} + Mo\textsuperscript{6+} $\leftrightarrow$ Fe\textsuperscript{3+} + Mo\textsuperscript{5+} mixed valence state. The spin-polarisation and magnetoresistance are highly sensitive to Fe and Mo cation inversion,$^{18-21}$ which introduces AF Fe-O-Fe and non-magnetic Mo-O-Mo linkages.\textsuperscript{17} Recently, Sr\textsubscript{2}FeMoO\textsubscript{6} has also attracted some interest for use as a fuel cell cathode.\textsuperscript{22} In terms of thermoelectric performance, Sr\textsubscript{2}FeMoO\textsubscript{6} is characterised by a low $S = -50 \mu V K^{-1}$ at 1073 K. However, this can be increased by partial
replacement of Sr by Ba ($S_{1073K} = -125 \mu V K^{-1}$), leading to $S^2/\rho$ values of 0.08 mW m$^{-1}$ K$^{-2}$ (Ref. 23). Measurements of the thermal conductivity showed a $1/T$ dependence characteristic of a crystalline solid but with a very low $\kappa = 0.2$ W m$^{-1}$ K$^{-1}$ at 1073 K, which resulted in $ZT = 0.3$ at 1073 K. This compares to $\kappa = 6$ W m$^{-1}$ K$^{-1}$ at high temperatures for SrTiO$_3$ with only Ti$^{4+}$ as a B-site cation. A note of caution is that the thermal conductivity measurements may have been affected by sample porosity, which is known to lead to significant underestimates of $\kappa$. Indeed, follow up studies on the Sr$_{2-x}$Ca$_x$FeMoO$_6$ and hole doped Sr$_{2-x}$K$_x$FeMoO$_6$ series (sample density 90-95%) gave high-temperature thermal conductivities between 2-4 W m$^{-1}$ K$^{-1}$. Nevertheless, it is interesting to explore the thermoelectric properties of Sr$_2$FeMoO$_6$ based systems further. Recent work from our group and others on A-site deficient SrTiO$_3$ led to the observation of two main effects: glass-like thermal conductivities (linear in T) for large concentrations of vacancies (27%) but also improved electrical conductivities for samples with a relatively low concentration of vacancies (7%). For these reasons, we undertook an investigation of nominally A-site deficient Sr$_{2-x}$FeMoO$_{6+\delta}$ compositions ($0 \leq x \leq 0.5$), where some oxygen deficiency is required to maintain electrically conducting samples (e.g. for $x = 0.5$ Fe$^{3+}$ and Mo$^{6+}$ are expected for $\delta = 0$). Our structure analysis demonstrates that the nominal A-site deficiency does not carry over into the final product of the reactions and instead a series of Mo-rich Sr$_2$Fe$_{1-y}$Mo$_{1+y}$O$_6$ double perovskites form.

**Experimental**

Polycrystalline Sr$_{2-x}$FeMoO$_6$ ($x = 0, 0.15, 0.25, 0.35$ and 0.5) samples were prepared using standard solid-state chemistry reactions. Stoichiometric amounts of SrCO$_3$, Fe$_2$O$_3$ and MoO$_3$ were mixed using a mortar and pestle, pressed into pellets and heated at 1350$^\circ$C in 5% H$_2$ in N$_2$ for 12 hr. The samples were then ground, re-pressed and sintered at 1400$^\circ$C in the same atmosphere for 4 hr. The heating and cooling rates were kept at 10 K/min. After the final reaction step, Fe flakes were observed on the surface of the pellets for the samples with $x > 0.15$. These were scraped off and the
pellets were lightly sanded. Laboratory X-ray powder diffraction (XRD) data were collected on a 
Bruker D8 Advance diffractometer with Cu K$_\alpha$ radiation. Room temperature time-of-flight neutron 
powder diffraction (NPD) data were collected on a 2 gram sample of the $x = 0.5$ composition on the 
GEM medium resolution diffractometer at the ISIS pulsed spallation neutron source, Rutherford 
Appleton Laboratory, UK. A multi-histogram (GEM detector banks 3–6) Rietveld fit to the NPD 
data was done using the GSAS and EXPGUI suite of programmes.\textsuperscript{30, 31} The microstructure was 
analysed using a Quanta 650 FEG ESEM equipped with an Oxford Instruments X-max 
150$^N$ detector for elemental mapping. The working distance, beam spot size and collecting time 
were 10 mm, 4.5mm and 120 sec respectively. The temperature dependence of the electrical 
resistivity and Seebeck coefficient were measured using Linseis LSR-3 instrument. The DC 
magnetic susceptibility (H=10 kOe) was measured using a Quantum Design MPMS vibrating 
sample magnetometer in the $2 \leq T \leq 400$K interval.

**Results**

**Composition and Structure:** The observation of Fe-flakes on the surface of some of the pellets and 
in the diffraction patterns (see below) strongly suggested that the composition of our perovskite 
samples had changed during high-temperature reaction under 5% H$_2$/N$_2$ atmosphere. This prompted 
further investigations using scanning electron microscopy (SEM), energy dispersive X-ray (EDX) 
elemental analysis and Rietveld analysis of X-ray and neutron powder diffraction data. The EDX 
measurements were performed on three random spots of ca. 8x9 µm for each sample, and the 
average values of the atomic ratios were used in the composition calculations. These results are 
summarized in Table 1 and reveal that a non-A-site deficient and Mo-rich Sr$_2$Fe$_{1-y}$Mo$_{1+y}$O$_6$ series 
has formed. The experimental compositions are as follows $y = 0$ (x = 0), 0.04 (x = 0.15), 0.08 (x = 
0.25), 0.13 (x = 0.35) and 0.20 (x = 0.5). In order to investigate the sample homogeneity in more 
detail, large area elemental maps (Sr, Fe and Mo) were collected for the $y = 0.2$ composition. The 
results are shown in Fig. 1. This demonstrates that all elements exhibit a homogeneous distribution,
indicating the product is free from macroscopic phase segregation. Some Fe-rich regions corresponding to iron particles are observed in the Fe map.

The room temperature XRD patterns for the Sr$_2$Fe$_{1-y}$Mo$_{1+y}$O$_6$ samples are shown in Fig. 2. The patterns for $0 \leq y \leq 0.13$ can be indexed using the tetragonal I4/m superstructure reported for Sr$_2$FeMoO$_6$, which allows for Fe/Mo rocksalt ordering, while the I4/mcm structure with a disordered B-cation arrangement was appropriate for $y = 0.2$. Both space groups correspond to the $a^0 a^0 c^{-}$ Glazer tilt system. A monotonic shift of the diffraction peaks to lower angles is observed and indicates a systematic expansion in the unit cell parameters as $y$-increases. The insets highlight the evolution of the (101) reflection that is a measure of the degree of Fe and Mo ordering, and the cluster of the (420), (332) and (116) reflections that can be seen to merge for larger $y$. The reduced (101) intensity signals a gradual loss of B-cation ordering, while the merging of the higher angle reflections shows a reducing tetragonal distortion. In addition to the major phase, there is also evidence for a minor iron impurity phase for $y \geq 0.08$.

Rietveld analysis of the XRD data was used to determine the distribution of the B-cations. These results are summarized in Table 1. Good fits were obtained using the compositions obtained from the elemental analysis with a gradual decrease in B-site ordering observed as the Mo content increases. In these refinements a full occupancy of the oxygen sites was assumed, and the oxygen positions were kept fixed at values reported for Sr$_2$FeMoO$_6$ (Ref. 35), and as determined from our neutron powder diffraction analysis on the $y = 0.2$ sample (see below). The fitted weight fractions of the Fe impurity are 0.54(1), 1.82(7) and 2.39(9) % for $y = 0.08, 0.13$ and 0.20. The evolution of the lattice parameters is given in Fig. 3. The linear changes in the unit cell parameters with composition were noted in an earlier study and our values are in excellent agreement with those published before. For example, for the c-axis a slope of 0.043Å/y was reported, while our slope is 0.045Å/y. In order to gain insight into the oxygen stoichiometry a 2 gram sample of the $y = 0.2$ sample was studied using neutron powder diffraction. The final Rietveld fit is shown in Fig. 4 and the refined unit cell and atomic parameters as well as selected bond distances and angles are

5
summarised in Table 2. The Rietveld fitting confirmed the assignment of the I4/mcm superstructure that was initially made based on X-ray diffraction. The refined composition is $\text{Sr}_2\text{Fe}_{0.784(2)}\text{Mo}_{1.216(2)}\text{O}_{5.996(1)}$ signalling a stoichiometric oxygen content, and an overall composition which is in excellent agreement with the EDX and XRD based compositions (Table 1). The observation of weak intensity in the (101) reflection at $d \approx 4.55 \text{ Å}$ in the neutron diffraction data (GEM Bank 3, Fig. 4) absent in the XRD patterns, indicated the presence of AF order at room temperature. The intensity was successfully fitted assuming a G-type ordering of a simple cubic Fe perovskite sublattice (e.g. as in LaFeO$_3$). The refined magnetic moment was 1.25(7) $\mu_B$ and is aligned along the crystallographic c-direction. Similar magnetic order has been observed previously in Fe-rich $\text{Sr}_2\text{Fe}_{1.33}\text{Mo}_{0.67}\text{O}_6$ ($T_N \approx 250 \text{ K}$) that contains a 1:1 ordering of Fe and ($\text{Mo}_{0.67}\text{Fe}_{0.33}$)$_3$, and in highly disordered $\text{Sr}_2\text{FeMoO}_6$ ($T_N \approx 750 \text{ K}$) with only 18% cation order. Ordered magnetic moments of 1.4 and 2.2 $\mu_B$/Fe atom were reported for these two compositions, respectively.

**Magnetic susceptibility**: The temperature and field dependences of the magnetisation ($M$) of the $y = 0.2$ sample are shown in Figure 5. The field dependence $M(H)$ (inset to Fig. 5) features a small hysteresis and is typical of a soft ferromagnet or a superparamagnet (small domain ferromagnet). This is in keeping with the presence of disrupted FIM Fe-O-Mo patches in this B-site disordered composition. The temperature dependence of the magnetisation $M(T)$ is compared to a sample of similar composition from the literature. A transition is evident at 250 K, in agreement with the literature data. The $M(T)$ data also reveal a substantial ferromagnetic background due to the presence of metallic Fe. A saturation magnetisation of 2 $\mu_B$/f.u ($M_{\text{sat}} = 25.9$ emu/gr) is reported for $\text{Sr}_2\text{Fe}_{0.8}\text{Mo}_{1.2}\text{O}_6$ whereas we observed a magnetization value of 37.3 emu/gr. Assuming that the difference is accounted for by elemental Fe ($M_{\text{sat}} = 221.7$ emu/gr), leads to an estimated 5.1 wt% of Fe in our sample. This is in good agreement with the values obtained from Rietveld analysis (Table 1 and 2).

**Thermoelectric properties**: The temperature dependence of $S$, $\rho$ and $S^2/\rho$ for the $\text{Sr}_2\text{Fe}_{1-y}\text{Mo}_{1+y}\text{O}_6$ samples are shown in Figure 6. The $S(T)$ curves have linear temperature dependences and vary
smoothly with composition (Figure 6a). The linear $S(T)$ is characteristic of a metal and the observed $S_{1000 K} = -55 \, \mu V \, K^{-1}$ for Sr$_2$FeMoO$_6$ is consistent with earlier reports.$^{23,25,26}$ The slope of the $S(T)$ curves was used to estimate the carrier concentration using $S = (8\pi k_B^2/3e^2) m^* (\pi/3n)^{2/3} T$, where $k_B$ is Boltzmann’s constant, $e$ is the electronic charge, $h$ is Planck’s constant, $m^*$ is the effective mass and $n$ is the carrier concentration.$^{41}$ An effective mass of 3.3$m_e$ was used in these calculations and the results are summarized in Table 1 and discussed below.$^{42,43}$ The magnitude of $S$ is reduced with increasing Mo content which is consistent with a transition to a metallic system that is also evident from the $\rho(T)$ data. The electrical resistivity for $y = 0$ decreases from ~ 100 m$\Omega$ cm at 300 K to 3 m$\Omega$ cm at 1000 K and shows two transitions at ~475 K and ~625 K (Figure 6b). Similar transitions were observed in the earlier report on the Sr$_{2-x}$Ba$_x$FeMoO$_6$ series.$^{23}$ The origin of these anomalies is not clear but it is worth noting the absence of any transitions in $S(T)$, suggesting that these may be due to extrinsic factors. The $y = 0.04$ and 0.08 samples contain signatures of these anomalies but for $y = 0.13$ and 0.20 smoothly varying metallic varying $\rho(T)$ were observed. The latter samples have $\rho_{300 K} \sim 0.5$ m$\Omega$ cm increasing to $\rho_{1000 K} \sim 1$ m$\Omega$ cm. It is possible that the semiconducting behaviour observed for the lower $y$ values is due to grain boundary effects that are suppressed at higher temperatures and with increased Mo content. The thermoelectric power factors are too small for these materials to be useful thermoelectrics with largest values of 0.11 and 0.04 mW m$^{-1}$ K$^{-2}$ at 1000 K for $y = 0$ and $y = 0.2$, respectively (Figure 6c).

**Discussion**

Elemental and structure analysis demonstrates that the nominal A-site deficient Sr$_{2-x}$FeMoO$_{6-\delta}$ compositions form a series of Mo-rich non-A-site deficient Sr$_2$Fe$_{1-y}$Mo$_{1+y}$O$_6$ perovskites under high-temperature (1350-1400 °C) and reducing conditions (5% H$_2$ in N$_2$). This suggests that these mixed Fe and Mo perovskites do not tolerate A-site and/or oxygen vacancies, at least under the employed synthetic conditions. It may be possible to stabilise the hypothetical Sr$_{0.5}$FeMoO$_6$ compound with Fe$^{3+}$ and Mo$^{6+}$ using soft chemistry methods and under oxidising atmospheres. This
would, however, involve losing the favourable electronic properties based on the Fe$^{2+/3+}$ and Mo$^{5+/6+}$ redox couple, leading to poor semiconducting or electrically insulating behaviour.

The Sr$_2$Fe$_{1-x}$Mo$_{1+y}$O$_6$ materials show a gradual transition from the largely B-site ordered $y = 0$ composition to the fully disordered $y = 0.2$ composition. One insightful way to think about these materials is not in terms of Fe/Mo ordering but in terms of the fractions of B-O-B’ linkages. This enables a comparison between samples with varying degrees of Fe/Mo ordering. The B-O-B’ fractions can be calculated from the refined B-site occupancies (Table 1). For example, the largely B-site ordered $y = 0$ composition has $0.9^2 + 0.1^2 = 0.82$ Fe-O-Mo linkages, $0.1 \times 0.9 = 0.09$ Fe-O-Fe and $0.1 \times 0.9 = 0.09$ Mo-O-Mo linkages, whereas the B-site disordered $y = 0.2$ sample has $2 \times 0.39 \times 0.61 = 0.48$ Fe-O-Mo linkages, $0.39^2 = 0.15$ Fe-O-Fe and $0.61^2 = 0.37$ Mo-O-Mo linkages. The composition dependence of the fractions of B-O-B’ linkages are shown in Figure 7. This reveals a gradual increase in the fraction of Mo-O-Mo linkages, demonstrating that the samples become more like SrMoO$_3$. In fact a linear extrapolation of the c-axis which is not affected by Glazer tilting (shown in the inset to Figure 3) leads to a good agreement with the value reported for cubic SrMoO$_3$. This suggests a gradual change in average B-cation oxidation state as $y$ is increased. Extrapolation of the unit cell volume or a-axis which are affected by changes in the octahedral tilt system leads to an overestimate for SrMoO$_3$. As intuitively expected, the increase in Mo-O-Mo linkages occurs at the expense of the Fe-O-Mo linkages; while an almost constant fraction of Fe-O-Fe linkages (0.1-0.15) are observed. This is somewhat unexpected as a-priori both Fe-O-Mo and Fe-O-Fe linkages could have been broken upon introduction of excess Mo, and suggests there may be an energetic or entropic stabilisation for the Fe-O-Fe linkages. The bottom panel of Figure 7 summarizes the 1000 K thermoelectric property data. This reveals a linear decrease of S, coupled to a decrease in $\rho$ as $y$ is increased, and is consistent with the observed transition to metallic behaviour as the Mo-O-Mo fraction is increased. The calculated charge carrier concentrations increase from $1.5 \times 10^{20}$ cm$^{-3}$ for $y = 0$ to $6.5 \times 10^{20}$ cm$^{-3}$ for $y = 0.2$ (Table 1). These are almost certainly an underestimate as the Hall carrier concentrations of single crystalline Sr$_2$FeMoO$_6$ are reported to be
Nevertheless, the trend of an increasing amount of charge carriers with y is clear. The metallic carrier concentrations also preclude the small iron impurities from having a significant impact on the thermoelectric properties, unlike in semiconductors where impurities can lead to substantial changes in carrier concentrations. Computational studies show that the introduction of excess Mo results in the presence of a Mo t_{2g} band at the Fermi level, which leads to the loss of the half-metallic conduction for y > 0.125. In other words, the Sr₂Fe₁₃₋₃Mo₁₊₃O₆ samples start to resemble non-magnetic SrMoO₃. The maximum power factors are ~ 0.1 mW m⁻¹ K⁻¹ which leads to an estimated upper limit ZT = 0.05 at 1000 K, using literature data for the thermal conductivity. The magnetic susceptibility and hysteresis for the y = 0.2 sample are in good agreement with the literature, and are typical of a ferrimagnet with small magnetic domains (a superparamagnet). The neutron data indicate G-type AF ordering at room temperature involving the Fe-O-Fe linkages of which there are about 15% in this composition. There is no evidence for long range FIM order coinciding with the AF order but further experiments below 250 K are needed to confirm the short range nature suggested by the susceptibility data. The observation of AF order at room temperature despite the small fraction of Fe-O-Fe linkages (below the percolation limit of 20-25%) suggests that this may be stabilised through Fe-O-Mo-O-Fe interactions, which could be ferromagnetic for Mo⁵⁺ or AF for non-magnetic Mo⁶⁺ cations. Evidence for the importance of Mo⁵⁺ comes from a comparison of the Neel temperatures of the Sr₂Fe(Fe₀.₃₃Mo₀.₆₇)O₆ (33% Fe-O-Fe) and disordered Sr₂FeMoO₆ (24% Fe-O-Fe) samples mentioned in the results section. The lowest T_N ~ 250 K is observed for Sr₂Fe(Fe₀.₃₃Mo₀.₆₇)O₆ which contains Fe³⁺/Mo⁶⁺ while the mixed valence Sr₂FeMoO₆ sample has T_N ~ 750 K, suggesting that the presence of Mo⁵⁺ is key to observe high Neel temperatures.

The results presented here suggest that these samples combine AF long range order (linked to Fe-O-Fe domains), short range FIM ordering (Fe-O-Mo domains) and itinerant electrons (Fe-O-Mo and Mo-O-Mo domains) all in one material. This may offer possibilities for the tuning and coupling of these properties in a single phase material.
Acknowledgements

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Table 1: SEM-EDX compositions, space group, lattice parameters, tetragonal distortion, Fe/Mo site occupancies, wt% iron impurities, Rietveld goodness of fit, carrier concentration (n) and percentage densities for the Sr$_2$Fe$_{1-y}$Mo$_{1+y}$O$_6$ (0 ≤ y ≤ 0.20) series.

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<td>0.85(3)/0.15(3)</td>
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<td>-</td>
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<td>89</td>
<td>90</td>
<td>90</td>
<td>85</td>
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I4/m: Sr: 4d (1/2, 0, 1/4); Fe/Mo: 2a (0, 0, 0); Mo/Fe: 2b (0, 0, 1/2); O1: 4e (0, 0, 0.252); O2: 8h (0.255, 0.249, 0).
I4/mcm: Sr: 4d (1/2, 0, 1/4); Fe/Mo: 4c (0, 0, 0); O1: 4a (0, 0, 0.25); O2: 8h (0.26, 0.76, 0).
Table 2: Refined crystallographic parameters and selected bond distances and angles for \( \text{Sr}_2\text{Fe}_{0.784(1)}\text{Mo}_{1.216(2)}\text{O}_{5.996(1)} \) from Rietveld fits against GEM neutron powder diffraction data.

<table>
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<th>Wyckoff position</th>
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<th>y</th>
<th>z</th>
<th>( U_{\text{iso}} (\text{Å}^2) )</th>
<th>Occupancy</th>
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Space group: I4/mcm; \( a=5.5845(3) \text{ Å}; c=7.9063(7) \text{ Å}; V=246.57(2) \text{ Å}^3 \)
Fe magnetic moment: \( m_x = m_y = 0, m_z = 1.25(7) \mu_B \)
**Figure 1:** (a) SEM micrograph and (b-d) EDX elemental distributions for the $y = 0.2$ sample from the $\text{Sr}_2\text{Fe}_{1-y}\text{Mo}_{1+y}\text{O}_6$ series.
**Figure 2:** Room temperature X-ray powder diffraction patterns for the Sr$_2$Fe$_{1-y}$Mo$_{1+y}$O$_6$ series. The insets highlight the decreasing intensity of the (101) superstructure reflection indicative of Fe/Mo rocksalt ordering, and the decreasing tetragonal distortion, respectively. The asterisk indicates a small Fe impurity.
Figure 3: Composition dependence of the lattice parameters for the \( \text{Sr}_2\text{Fe}_{1-y}\text{Mo}_{1+y}\text{O}_6 \) series. The inset shows the interpolation of the lattice parameters up to \( y = 1 \), the \( \text{SrMoO}_3 \) lattice parameter was taken from Ref. 45.
**Figure 4:** Observed (solid blue circles), calculated (red line) and difference (green line) Rietveld profiles for room temperature neutron powder diffraction data collected on Sr$_2$Fe$_{0.8}$Mo$_{1.2}$O$_6$. Bragg reflection markers correspond to the main phase, nuclear and magnetic contributions, and a 1.5 wt%. Fe impurity (top to bottom). The prominent (101) magnetic reflection is indicated by the green arrow.
Figure 5. Temperature dependence of the magnetization for Sr$_2$Fe$_{0.8}$Mo$_{1.2}$O$_6$. Data on a sample of similar composition from Ref. 37 is included for comparison. The inset shows the M(H) hysteresis loop at 2K.
Figure 6: Temperature dependence of (a) the Seebeck coefficient ($S$), (b) the electrical resistivity ($\rho$) and (c) the thermoelectric power factor ($S^2/\rho$) for the $\text{Sr}_2\text{Fe}_{1-y}\text{Mo}_{1+y}\text{O}_6$ series.
Figure 7: Comparison of (a) the changes in structure quantified using the fraction of B-O-B’ linkages and (b) the thermoelectric properties for the Sr$_2$Fe$_{1-y}$Mo$_1+y$O$_6$ ($0 \leq y \leq 0.20$) series.
References

A-site deficiency does not survive in $\text{Sr}_{2-x}\text{FeMoO}_6$ and instead Mo-rich $\text{Sr}_2\text{Fe}_{1-y}\text{Mo}_{1+y}\text{O}_6$ perovskites, characterised by the gradual disordered of Fe and Mo, form.