

Topochemical nitridation of Sr₂FeMoO₆

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Supplementary Information

Experimental Details

Sr₂FeMoO₆ was prepared by using the citrate sol-gel method.¹ Stoichiometric amounts of Sr(NO₃)₂ (Aldrich, 99 %), Fe(NO₃)₃·9H₂O (Aldrich, 99.95 %) and (NH₄)₆Mo₇O₂₄·4H₂O (Aldrich, 99.98 %) were dissolved in H₂O, and an excess of C₆H₈O₇ (citric acid, Aldrich 99 %, 2 moles per mole of Sr₂FeMoO₆) was subsequently added to the solution. The solutions were evaporated at 80 °C with continuous stirring and the resulting powders were subsequently treated in synthetic air (Carbueros Metálicos, 99.999 %) at 500 °C and 800 °C for 2 hours at each temperature. The obtained mixture of oxides SrMoO₄ and SrFeO_{3-x} was treated at 1100 °C in Ar/H₂ 99/1 (V/V, Air Liquide, 99.995 %) during two cycles of 12 hours with intermediate regrinding. Reactions under NH₃ (Carbueros Metálicos, 99.9%) were performed starting with Sr₂FeMoO₆ or with the mixture SrFeO_{3-x} and SrMoO₄, at temperatures between 500 and 650 °C, using flow rates of 600 and 1000 cm³/min and treatment times between 6 and 12 hours. The oxynitride Sr₂FeMoO_{4.9}N_{1.1} was prepared by treatment of 150 mg of Sr₂FeMoO₆ under NH₃ flow of 1000 cm³/min at 575 °C during 6 hours. Energy dispersive X-ray spectroscopy analyses of ca. 10 crystallites in this sample gave average Sr/Mo and Fe/Mo ratios of 1.90(13) and 0.97(7) respectively.

N contents were determined by combustion analysis in a Thermo Fisher Scientific instrument, heating the samples in oxygen up to 1060 °C and using MgO, WO₃ and Sn as additives and atropine as a reference standard. EDS analyses of cation contents were performed in a FEI Quanta 200 FEG scanning electron microscope equipped with a EDAX detector with an energy resolution of 132 eV.

Laboratory X-ray powder diffraction data were collected on a Panalytical X'Pert Pro MPD diffractometer using Cu K α radiation (λ = 1.5418 Å). High resolution synchrotron X-ray powder diffraction data were measured from capillary (0.5 mm diameter) samples in the angular range 3.0° ≤ 2 θ ≤ 50.0° at the MSPD beamline² of the ALBA Synchrotron (Cerdanyola del Vallès, Spain). Using a double Si (111) and Si (220) crystal monochromator, a short wavelength was selected and calibrated with Si NIST (λ = 0.41322 Å for Sr₂FeMoO₆ and 0.41269 Å for Sr₂FeMoO_{4.9}N_{1.1}). Rietveld analysis was carried out using the program Fullprof.³ Background refinement was performed by linear interpolation and the data were corrected for absorption.

Neutron powder diffraction data were collected for Sr₂FeMoO_{4.9}N_{1.1} and Sr₂FeMoO₆ at 90 K on the D20 diffractometer at the Institut Laue-Langevin (ILL), Grenoble, using 80 mg of sample placed in a vanadium can. A high take-off angle of 118° produced neutrons with a wavelength of 1.86502 Å. A series of additional scans between 5 K and 450 K were taken on the oxynitride using a take-off angle of 90° giving λ =1.5423 Å. Powder diffraction data were analysed using the FullProf software package.

Electron diffraction micrographs were obtained in a JEOL 1210 transmission electron microscope operating at 120 kV, equipped with a side-entry 60°/30° double tilt GATAN 646 specimen holder. The samples were prepared by dispersing the powders in hexane and depositing a droplet of this suspension on a holey carbon film supported on a copper grid.

Magnetic measurements were performed at fields of 3000 to 11000 G between 2 K and 400 K using a Quantum Design SQUID magnetometer. Magnetization-field loops were measured between -7 and +7 T at 2, 5, 35, 100 and 300 K. Mössbauer spectra were acquired at room temperature using a conventional transmission Mössbauer spectrometer with a $^{57}\text{Co}/\text{Rh}$ source. The source was moved at constant velocity and the γ counts were collected in a 512 multichannel analyzer. Velocity calibration was done using a 25- μm thick metallic Fe foil. The spectra were fitted to 2 doublets that were assigned to Fe(III) and Fe(IV).

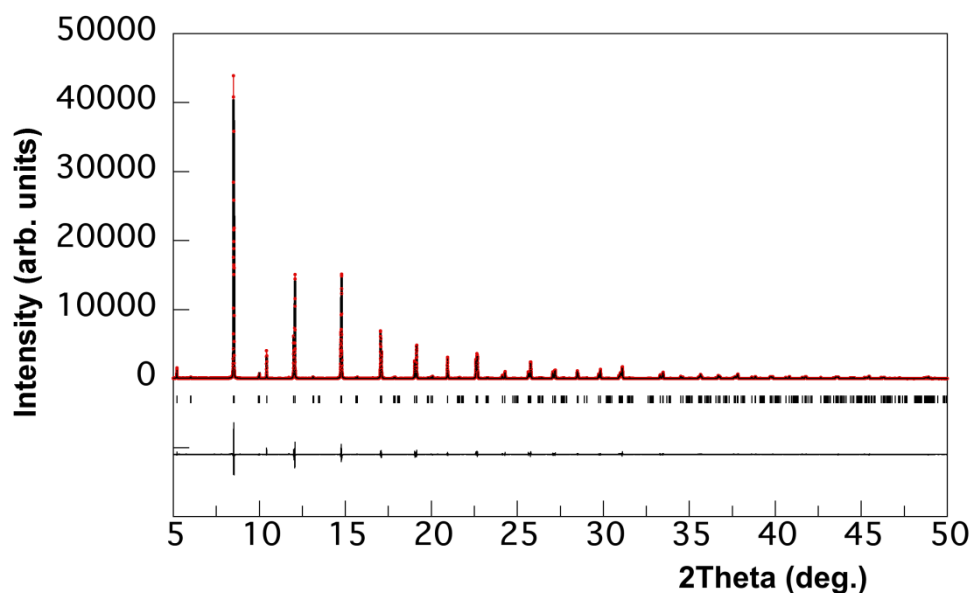


Figure S1. Observed and calculated synchrotron X-ray powder diffraction patterns ($\lambda=0.41322$ Å) at 90 K for $\text{Sr}_2\text{FeMoO}_6$ refined in the space group $I4/m$.

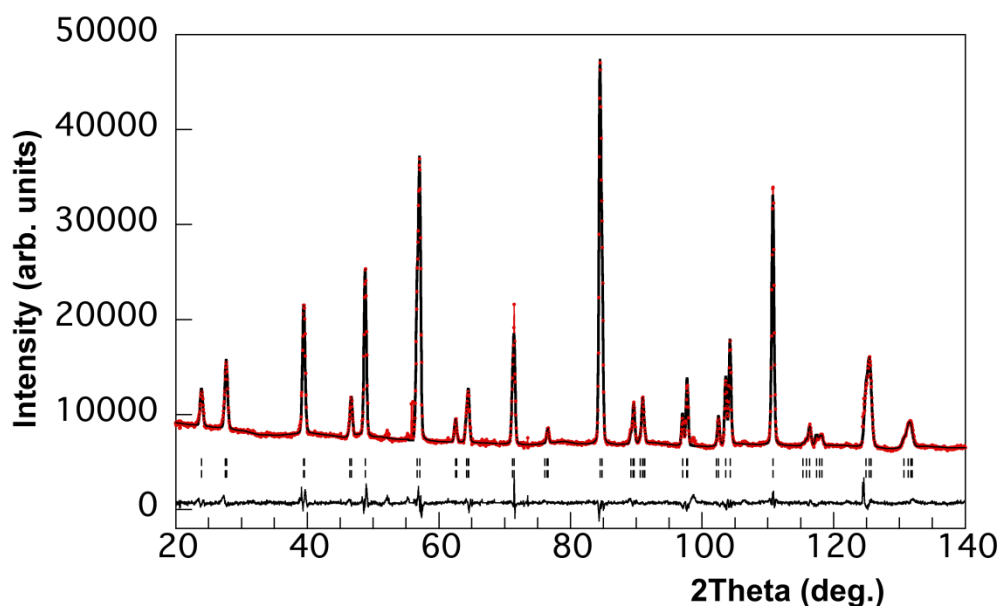


Figure S2. Observed and calculated neutron powder diffraction patterns ($\lambda= 1.86502$ Å) at 90 K for $\text{Sr}_2\text{FeMoO}_6$ refined in the space group $I4/m$. The two set of Bragg position marks stand for nuclear and magnetic reflections.

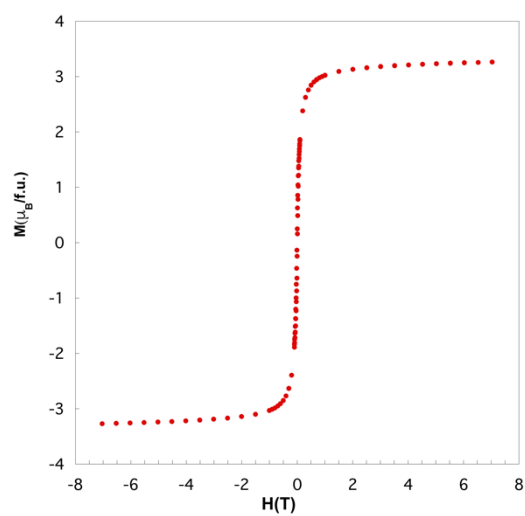


Figure S3. The M-H hysteresis loop of $\text{Sr}_2\text{FeMoO}_6$ sample at $T=2$ K.

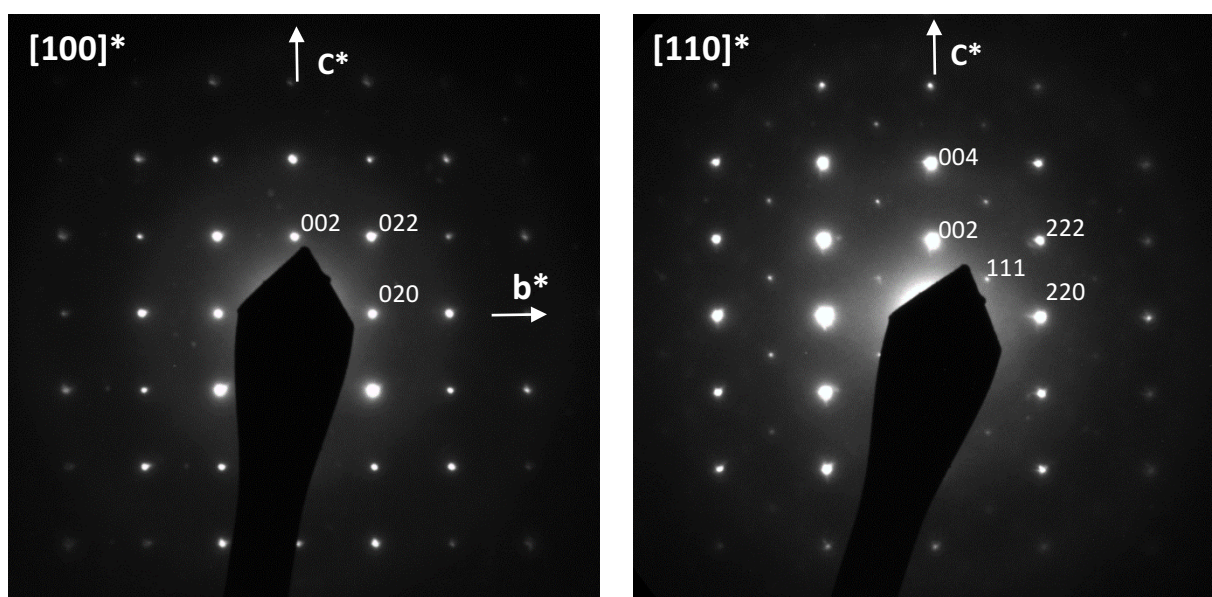


Figure S4. Electron diffraction patterns along $[100]$ and $[110]$ zone axes of $\text{Sr}_2\text{FeMoO}_{4.9}\text{N}_{1.1}$ indexed in the unit cell $2 a_p \times 2 a_p \times 2 a_p$.

Disentangle of ferromagnetic and paramagnetic contributions

Neutron diffraction patterns of the oxynitride sample showed only a very small contribution from magnetic diffraction. Figure S5 shows the evolution with temperature of the 101 reflection of the $\text{Sr}_2\text{FeMoO}_6$ phase present in the sample in a proportion of c.a. 10 %. It can be observed that this intensity starts to grow at temperatures below 400 K, nearby the Curie point of the oxide showing that the magnetic diffraction is due to this phase.

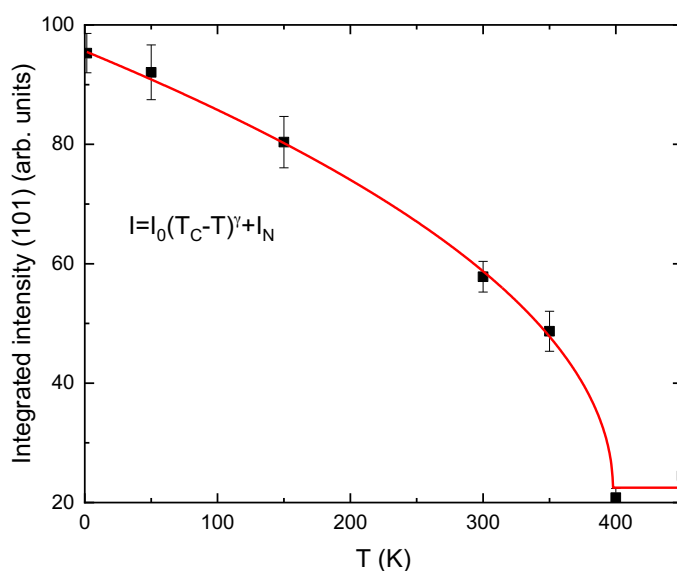


Figure S5: Evolution with temperature of the integrated intensity of 101 diffraction peak of $\text{Sr}_2\text{FeMoO}_6$ phase in the oxynitride sample. The red curve shows the fitting of the expected critical behavior of the magnetic moment.

In order to study the magnetism of $\text{Sr}_2\text{FeMoO}_{4.9}\text{N}_{1.1}$, it is necessary to separate the contributions from the oxide and the oxynitride. This is done following the strategy previously reported.^{4,5} We assumed that the total magnetic moment of the sample has two contributions, one ferromagnetic (attributed to the oxide phase), that should not depend on the applied magnetic field when the sample is far enough from the Curie point, and a second one that is paramagnetic (attributed to the oxynitride) and thus proportional to the applied field: $M(T, H) = M_{\text{ox}}(T) + \chi_{\text{ON}}(T) \cdot H$. In order to separate the two contributions, we exploit this different field dependence. We measured the $M(T)$ curves under different applied magnetic fields ($H = 3, 5, 7, 9$ and 11 kOe), and construct the $M(H)$ curves for every temperature (an interpolation procedure was performed to homogenize the temperature points). Further, we fit the above expression for every temperature. Figure S6(a) shows some examples of this fitting for representative temperatures. It can be seen that the points measured at 3 kOe deviate considerably from the linear behavior hence they have been excluded from the fitting.

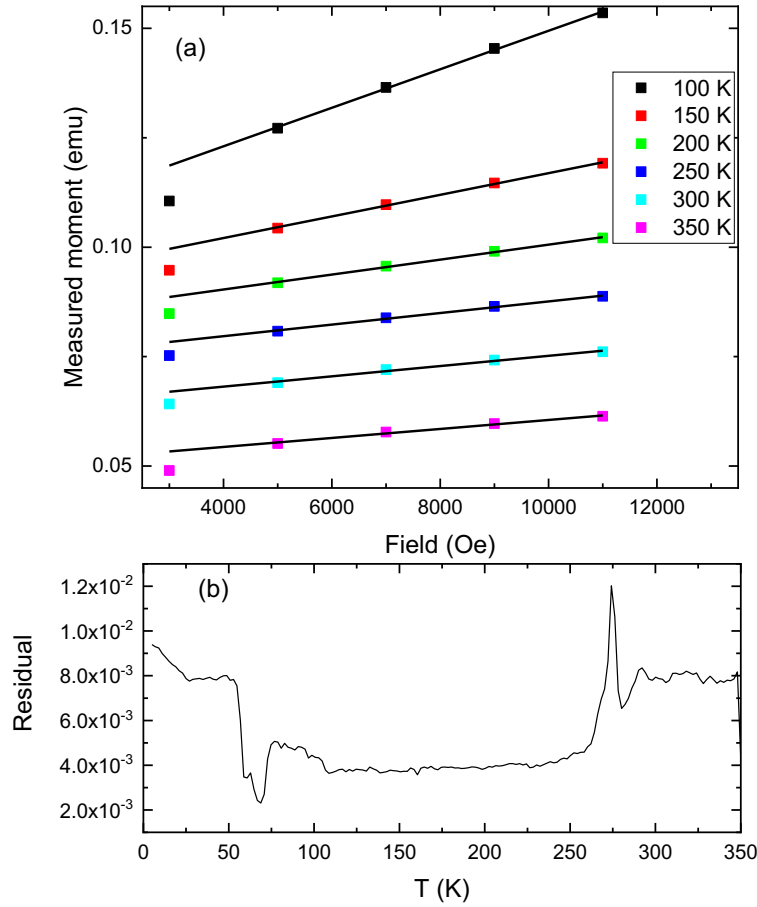


Figure S6 (a) Plot at some selected temperatures of the M vs H curves. The linear fittings are plotted as lines. (b) Residual of the fitting as a function of temperature.

The quality of the fitting has been evaluated by means of the residual R

$$R(T) = \left[\sum_{fields} \left(\frac{M_{OX}(T) + \chi_{ON}(T)H}{M(T, H)} - 1 \right)^2 \right]^{1/2}$$

The residual is plotted in Figure S6(b) and in the region where the inverse of χ_{ON} follows a linear behavior it is around 4.0×10^{-3} .

Table S1. Fractional atomic coordinates in space group I4/m, cation and anion occupancies and isotropic temperature factors for Sr₂FeMoO₆ from the refinement to synchrotron diffraction data at 90 K using $\lambda= 0.41322 \text{ \AA}$.^(a)

| Atom | Wyckoff site | x | y | z | B(Å ²) | Occ. factor |
|----------|--------------|-----------|----------|-----------|--------------------|----------------|
| Sr | 4d | 0.5 | 0 | 0.25 | 0.27(1) | 1 |
| Fe1/ Mo1 | 2a | 0 | 0 | 0 | 0.22(3) | 0.888(1)/0.112 |
| Fe2/Mo2 | 2b | 0 | 0 | 0.5 | 0.08(2) | 0.112/0.888 |
| O1 | 8h | 0.2311(8) | 0.277(1) | 0 | 0.44(5) | 1 |
| O2 | 4e | 0 | 0 | 0.2546(4) | 0.44 | 1 |

(a) Estimated standard deviations in parentheses are shown once for each independent variable. Fe/Mo occupation factors were refined subject to the ideal stoichiometry. Refined cell parameters were a= 5.55568(1), c=7.90604(2) Å. Agreement factors: $\chi^2=1.98$; $R_{wp}= 17.1 \%$; $R_{Bragg}= 4.72 \%$.

Table S2. Fractional atomic coordinates in space group I4/m, cation and anion occupancies and isotropic temperature factors for Sr₂FeMoO₆ from the refinement to neutron diffraction data at 90 K using $\lambda= 1.86502 \text{ \AA}$.^(a)

| Atom | Wyckoff site | x | y | z | B(Å ²) | Occ. factor |
|----------------|--------------|-----------|------------|-----------|--------------------|----------------|
| Sr | 4d | 0.5 | 0 | 0.25 | 0.26(3) | 1 |
| Fe1/ Mo1 | 2a | 0 | 0 | 0 | 0.08(2) | 0.888(1)/0.112 |
| Fe2/Mo2 | 2b | 0 | 0 | 0.5 | 0.08 | 0.112/0.888 |
| O1 | 8h | 0.2256(2) | 0.2744(2) | 0 | 0.43(2) | 1 |
| O2 | 4e | 0 | 0 | 0.2580(7) | 0.43 | 1 |
| Bond Length(Å) | Sr-O1 (x4) | 2.6522(7) | Sr-O1 (x4) | 2.9216(7) | Sr-O2 (x4) | 2.7757(2) |
| | Fe-O1 (x4) | 1.972(1) | Fe-O2 (x2) | 2.037(6) | | |
| | Mo-O1 (x4) | 1.972(1) | Mo-O2 (x2) | 1.912(6) | | |

(a) Estimated standard deviations in parentheses are shown once for each independent variable. Fe/Mo occupation factors were refined subject to the ideal stoichiometry. Refined cell parameters were a= 5.5499(3), c=7.8975(4) Å. Agreement factors: $\chi^2=3.19$; $R_{wp}= 2.52 \%$; $R_{Bragg}= 3.16 \%$

Table S3. Fractional atomic coordinates in space group Fm-3m, cation and anion occupancies and isotropic temperature factors for Sr₂FeMoO_{4.9}N_{1.1} from the refinement to synchrotron diffraction data at 90 K using $\lambda = 0.41230 \text{ \AA}$.^(a)

| Atom | Wyckoff site | x | y | z | B(Å ²) | Occ. factor |
|----------|--------------|-----------|------|------|--------------------|----------------|
| Sr | 8c | 0.25 | 0.25 | 0.25 | 0.97(2) | 1 |
| Fe1/ Mo1 | 4a | 0 | 0 | 0 | 0.78(4) | 0.825(1)/0.175 |
| Fe2/Mo2 | 4b | 0.5 | 0.5 | 0.5 | 1.10(3) | 0.175/0.825 |
| O1/N1 | 24e | 0.2495(5) | 0 | 0 | 0.82(4) | 0.817/0.183 |

(a) Estimated standard deviations in parentheses are shown once for each independent variable. Fe/Mo occupation factors were refined subject to the ideal stoichiometry. Refined cell parameters were $a = 7.87774(2) \text{ \AA}$. Agreement factors: $\chi^2 = 2.64$; $R_{wp} = 10.8 \%$; $R_{Bragg} = 2.53 \%$.

¹ D.Sánchez, J.A.Alonso, M.García-Hernández, M.J.Martínez-Lope and M.T.Casais, *J. Phys. Condens. Matter*. 2005, **17**, 3673.

² F. Fauth, I. Peral, C. Popescu, C. and M. Knapp, M. *Powder Diffraction* 2013, **28**, S360.

³ J.Rodríguez-Carvajal, *Phys. B*, 1993, **192**, 55.

⁴ J. Navarro, Ll. Balcells, B. Martínez and J. Fontcuberta, *J. Appl. Phys.* 2001, **89**, 7648.

⁵ B. Martínez, J. Navarro, Ll. Balcells and J. Fontcuberta, *J. Phys.: Cond. Matter* 2003, **12**, 10515.