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Topochemical synthesis of cation ordered double perovskite oxynitrides

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Supplementary information

Experimental Details

1.5 g of cation ordered Sr_2FeWO_6 was prepared by using the citrate sol-gel method. [S1] Stoichiometric amounts of $Sr(NO_3)_2$(Aldrich, 99 %), $Fe(NO_3)_3 \cdot 9H_2O$ (Aldrich, 99.95 %) and $(NH_4)_6H_2W_{12}O_{40} \cdot 3H_2O$ (Aldrich, 99.99 %) were dissolved in H_2O, and an excess of $C_6H_8O_7$ (citric acid, Aldrich 99.5 %, 2 moles per mole of Sr_2FeWO_6) was subsequently added to the solution. The solutions were evaporated at 80 °C with continuous stirring and the resulting powders were subsequently treated in air at 500 °C and 800 °C for 2 hours to form the mixture of oxides $SrWO_4$ and $SrFeO_{3-x}$. This mixture was treated at 1000 °C in Ar/H_2 95/5 (V/V, Carburos Metálicos, 99.995 %) during 6 hours leading to the cation ordered compound Sr_2FeWO_6. The cation ordered oxynitrides $Sr_2FeWO_{5+x}N_{1-x}$ $(0< x \leq 1)$ were prepared by treatment of 200 mg of Sr_2FeWO_6 under $NH_3(g)$ flow of 100 to 1000 cm^3/min (Carburos Metálicos, 99.9%) at temperatures between 600 and 660 °C. The reaction times at the maximum temperature were between 6 and 12 hours. Longer treatments induced the decomposition of the oxynitride with formation of Sr_3WO_6. Cation disordered $Sr(Fe_{0.5}W_{0.5})O_{2.4}N_{0.6}$ was prepared by ammonolysis of the mixture of $SrWO_4$ and $SrFeO_{3-y}$ at 650 °C.

N contents were determined by combustion analysis in oxygen in a Thermo Fisher Scientific instrument, heating the samples in oxygen up to 1060 °C and using MgO, WO_3 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 Kα radiation (λ= 1.5418 Å). High resolution synchrotron X-ray powder diffraction data at room temperature were measured from capillary (0.5 mm diameter) samples in the angular range $3.0^\circ \leq 2\theta \leq 45.0^\circ$ at the MSPD beamline[S2] 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 = 0.41269 Å). The data for the sample with composition $Sr(Fe_{0.5}W_{0.5})O_{2.4}N_{0.6}$ were acquired using a PSI detector and λ= 0.619714 Å. Rietveld analysis was carried out using the program Fullprof.[S3] Background refinement was performed by linear interpolation and the data were corrected for absorption.

Neutron powder diffraction data for Sr_2FeWO_5N between 1.8 K and 50 K were collected on the D20 diffractometer at the Institut Laue-Langevin (ILL), Grenoble, using 80 mg of sample placed in a vanadium can. The neutron wavelengths for the 50 K data were 1.12 and 1.54 Å. A series of scans were taken at intervals of approximately 2.5 K between 1.8 K and 50 K, using λ=1.54 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 H=5000 G between 2 K and 400 K using a Quantum Design SQUID magnetometer. Mössbauer spectra were acquired at room temperature using a conventional transmission Mössbauer spectrometer with a ^{57}Co/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 2-3 doublets that were assigned to Fe(II), Fe(III) and antisite Fe(III). Some parameters shown in Table S2 were set to fixed values because of strong correlation arising from the overlapping of the doublets in the spectra.

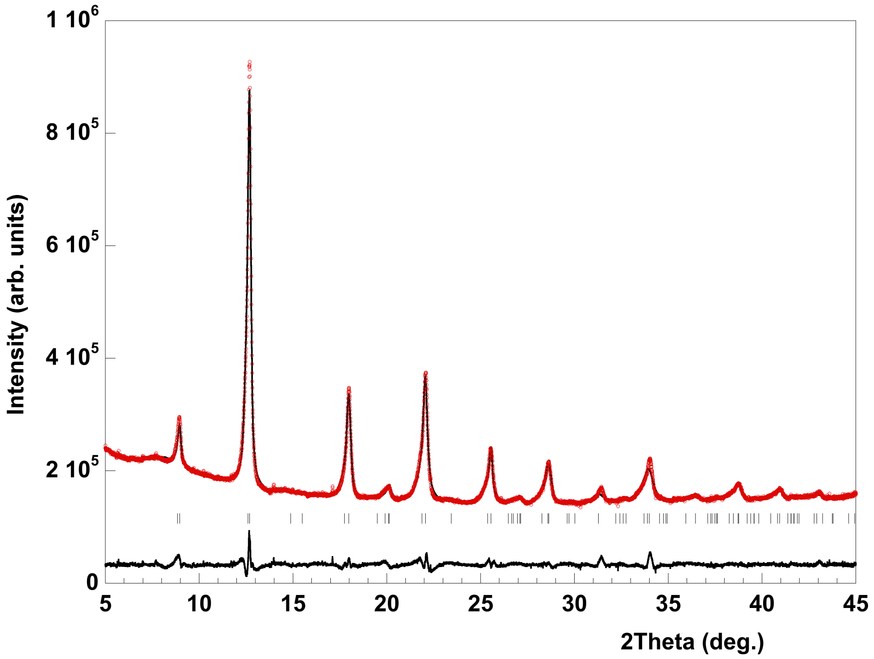

Figure S1. Observed and calculated synchrotron X-ray powder diffraction patterns (λ=0.619714 Å) at room temperature for cation disordered $Sr(Fe_{0.5}W_{0.5})O_{2.4}N_{0.6}$ obtained by treatment of a 1:1 mixture of $SrWO_4$ and $SrFeO_{3-x}$ under NH_3 flow of 200 cm^3/min at 650 °C. The structure was refined in the space group I4/mcm with cell parameters a=5.60273(16), c=8.0349(6) Å. Agreement factors: χ^2=7.20; R_{wp}= 1.93 %; R_{Bragg}=2.44 %.

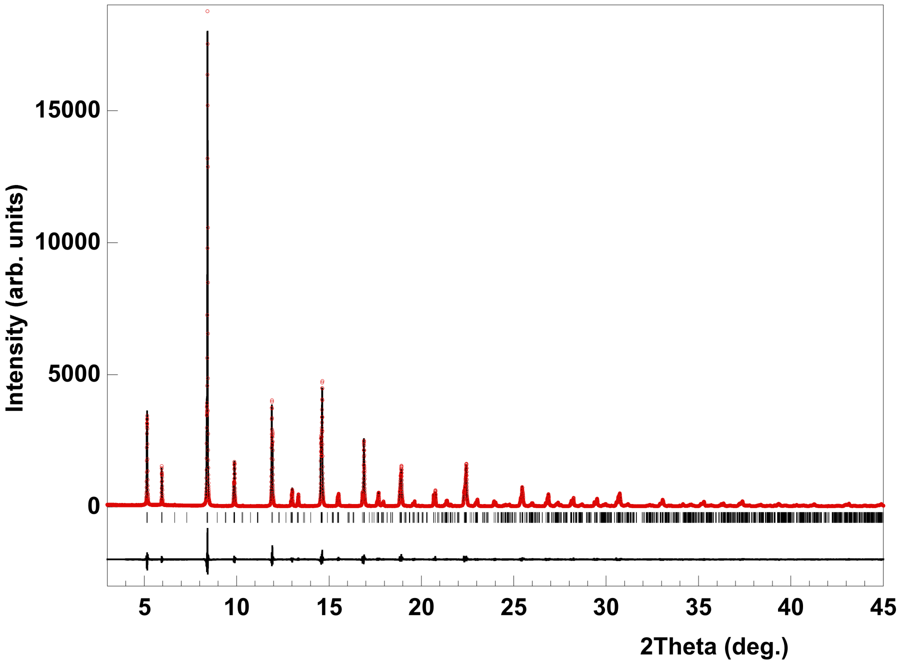

Figure S2. Observed and calculated synchrotron X-ray powder diffraction patterns (λ=0.41269 Å) at room temperature for $Sr_2FeWO_{5.8}N_{0.2}$ refined in the space group $P2_1/n$.

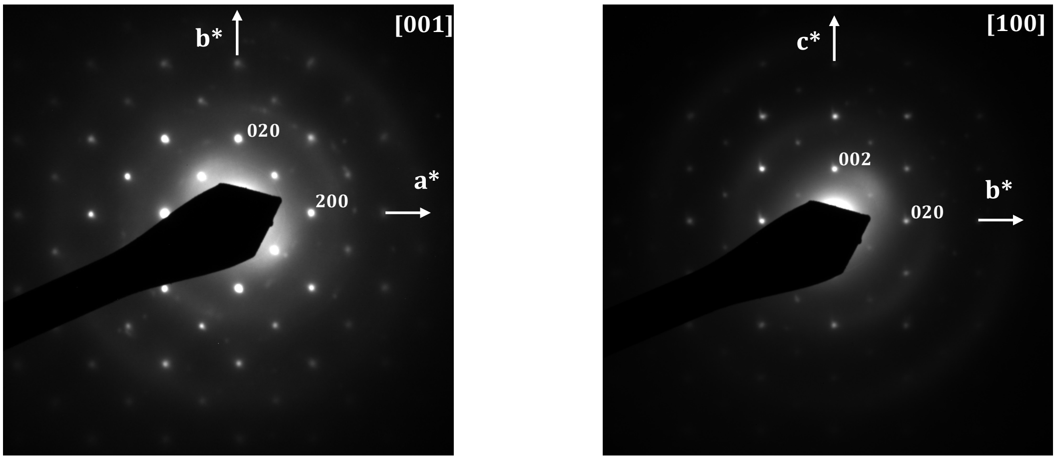

Figure S3. Electron diffraction patterns along [001] and [100] of Sr_2FeWO_5N.

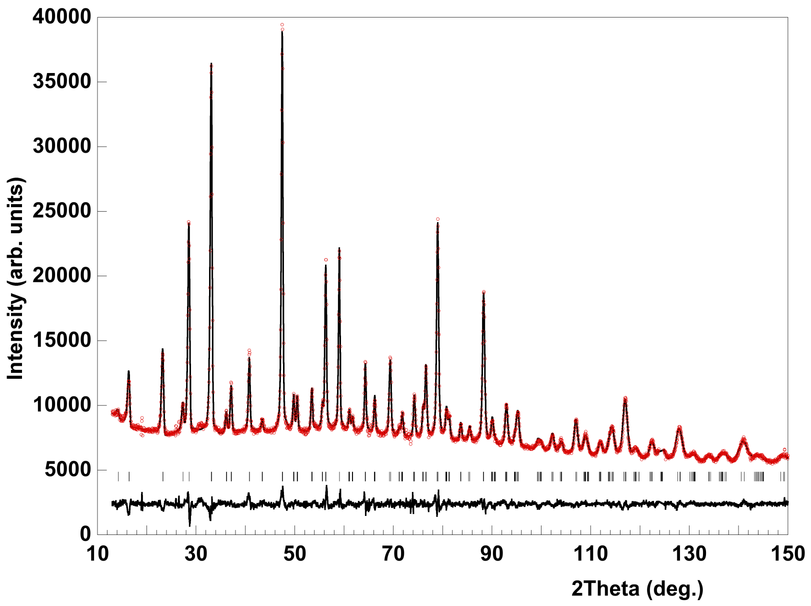

Figure S4. Observed and calculated neutron powder diffraction patterns at 50 K (λ=1.12 Å) for Sr_2FeWO_5N.

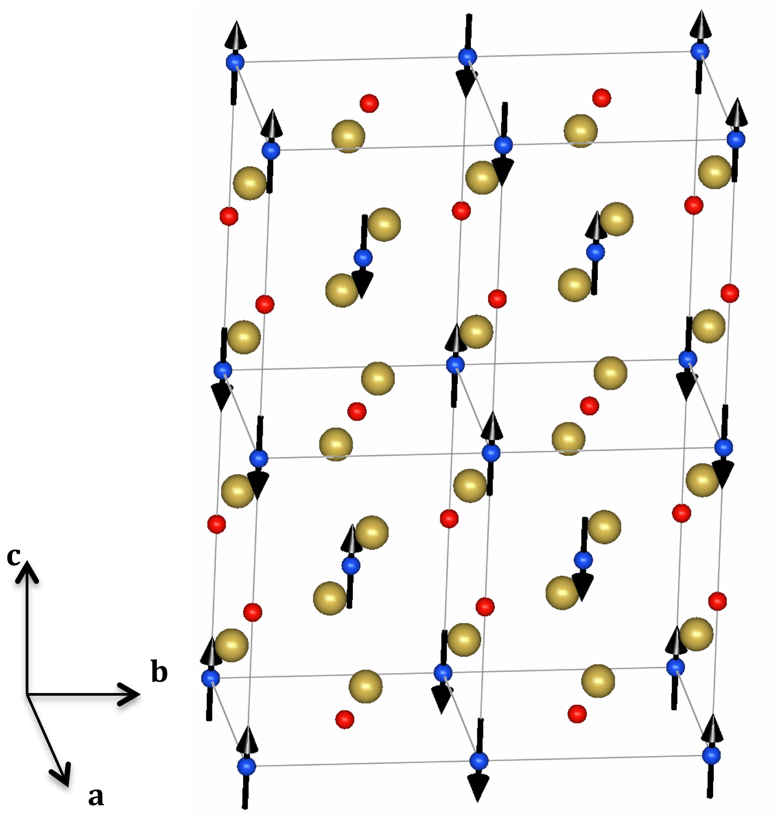

Figure S5. Magnetic Structure of Sr_2FeWO_5N determined at 1.8 K. Fe, W and Sr atoms are depicted as blue, red and yellow spheres respectively.

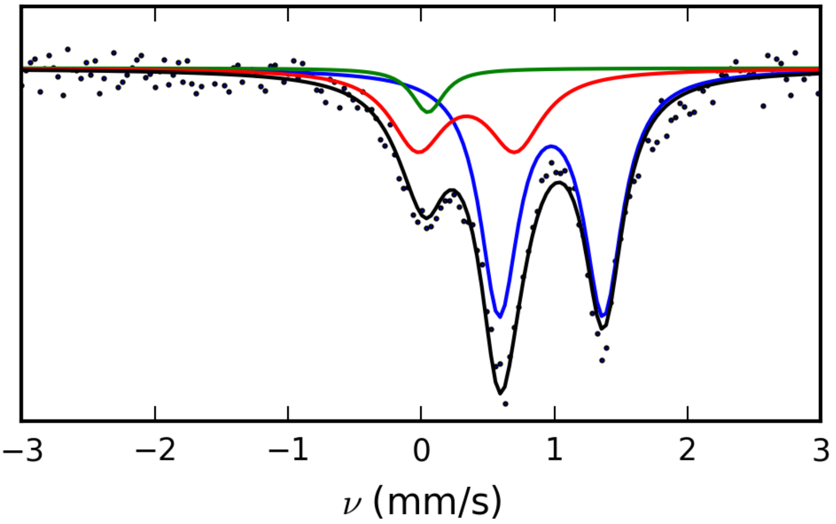

Figure S6. Mössbauer spectra of $Sr_2FeWO_{5.8}N_{0.2}$ observed at 295 K showing the contributions of Fe(II) , Fe(III) and antisite Fe(III) as blue, red and green lines respectively.

Table S1. Atomic coordinates in monoclinic space group $P2_1/n$, cation and anion occupancies and isotropic temperature factors for $Sr_2FeWO_{5.8}N_{0.2}$ from the refinement to synchrotron powder diffraction data at room temperature using λ= 0.41269 Å.[a]

Atom	Wyckoff Site	x	y	z	B(Å^2)	Occ. factor
Sr	4e	0.9984(6)	0	0.24992(16)	0.789(7)	1
Fe1/ W1	2d	0.5	0	0.5	0.411(16)	0.982(5)/ 0.018
Fe2/W2	2b	0.5	0	0	0.331(4)	0.018/0.982
O1/N1	4e	0.0477(13)	0.5384(17)	0.2554(9)	0.48(7)	0.967/0.033
O2/N2	4e	0.7190(14)	0.2543(17)	0.0092(19)	0.48	0.967/ 0.033
O3/N3	4e	0.2464(16)	0.2291(18)	0.9689(14)	0.48	0.967/ 0.033

(a) Estimated standard deviations in parentheses are shown once for each independent variable. Fe/W occupation factors were refined subject to the ideal stoichiometry. Anion occupancies were not refined. Refined cell parameters were a=5.6474(1), b=5.6131(1), c=7.9369(2) Å, β=89.96(5) °. Agreement factors: χ^2=2.97; R_{wp}= 8.19 %; R_{Bragg}=2.43 %.

Table S2. Mossbauer parameters of $Sr_2FeWO_{6-x}N_x$ samples[a]

N/formula		δ^b (mm/s)	Δ^c (mm/s)	FWHM[d] (mm/s)	A[d] (%)
0					
	Fe(II)	1.098(2)	0.729(4)	0.289(5)	93(1)
	Anti	0.164	0.34(4)	0.28(7)	7(1)
0.29					
	Fe(II)	1.091(4)	0.782(8)	0.346(11)	65(2)
	Fe(III)	0.454	0.73(3)	0.50(6)	30(2)
	Anti	0.164	0.0(2)	0.28	5
0.63					
	Fe(II)	0.98(1)	1.04(2)	0.72(3)	43(1)
	Fe(III)	0.449(3)	0.651(7)	0.41(1)	52(1)
	Anti	0.164	0.45(4)	0.28	5
1.03					
	Fe(III)	0.443(6)	0.574(8)	0.55(2)	95(1)
	Anti	0.164	0.11(8)	0.28	5(1)

(a)Parameters without standard deviation in parentheses were set to fixed values; (b) isomer shift relative to α-Fe, (c) quadrupole splitting, (d) full width at half maximum, (e) relative area.

References

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S2 F. Fauth, I. Peral, C. Popescu, C. and M. Knapp, M. *Powder Diffraction* **28**, S360 (2013).

S3 J.Rodríguez-Carvajal, *Phys. B*, 1993, **192**, 55.