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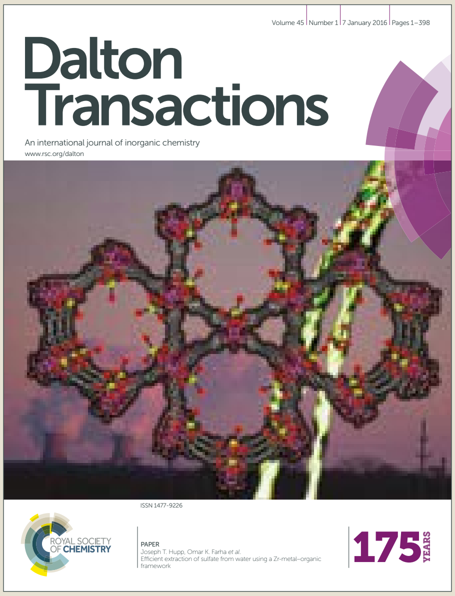

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Topochemical synthesis of cation ordered double perovskite oxynitrides

Roberta Ceravola,[a] Judith Oró-Solé,[a] Ashley. P. Black,[a] Clemens Ritter,[b] Inés Puente Orench [b,c] Ignasi Mata,[a] Elies Molins,[a] Carlos Frontera[a] and Amparo Fuertes[*, a]

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Topochemical nitridation in ammonia at moderate temperatures of cation ordered Sr_2FeWO_6 produces new antiferromagnetic double perovskite oxynitrides $Sr_2FeWO_{6-x}N_x$ with $0<x\leq 1$. Nitrogen introduction induces the oxidation of Fe^{2+} to Fe^{3+} and decreases T_N from 38 K (x=0) to 13 K for Sr_2FeWO_5N which represents the first example of a double perovskite oxynitride with both high cationic order and nitrogen content. The synthetic approach can be extended to other cation combinations expanding the possibility of new materials in the large group of double perovskites.

Transition metal oxynitride perovskites $ABO_{3-x}N_x$ (A = alkaline metal or lanthanide) are emergent materials showing tunable colour,[1] high dielectric constants,[2] photocatalytical activity under visible light, [3] colossal magnetoresistance (CMR), [4, 5] and ferroelectricity[6] among other properties. [7] They have been reported for M = Ti, Zr, V, Cr, Nb, Ta, Mo and W in high oxidation states, and properties may be tuned by controlling the N/O ratio, e.g. colour in $Ca_{1-x}La_xTaO_{3-x}N_x$,[1] CMR in $EuWO_{3-x}N_x$[5] or the transition temperature in antiferromagnetic $LnCrO_{3-x}N_x$ (Ln=La, Pr, Nd).[8]

Double perovskite oxides $A_2B'B''O_6$ show a large diversity of properties that are tuned by the d states of the transition metals and their degree of order in the B sites among other factors. Cation order is determined by differences in charge and size of the transition metals and may affect the physical properties.[9] Iron double perovskites with formula $A_2FeB''O_6$ are important materials because of ferromagnetism at high temperature ($T_C \approx 400$ K), colossal magnetoresistance and half-metallic properties found in Sr_2FeMoO_6.[10] The analogous compound Sr_2FeWO_6 is antiferromagnetic with a Néel temperature (T_N) of 38 K.[11] Both compounds show Fe/B'' order degrees higher than 90 % which is crucial for long order exchange coupling between the magnetic cations.

Double perovskite oxynitrides have been scarcely investigated. They have been only reported for $Sr_2FeMoO_{5.7}N_{0.3}$ which is cation ordered but poorly nitrided, Sr_2FeMoO_5N that shows a high disorder degree,[12] and $LaMg_{1/3}Ta_{2/3}O_2N$ that has been reported to show a low degree of order although precise structural data on this compound have not been yet published.[13,14] The synthetic methods used for the preparation of these oxynitrides were the treatment in NH_3 at moderate to high temperatures of mixtures of oxides. Increasing the temperature may enhance the cation order but also induces the reduction of the transition metals then decreasing the nitrogen content. On the other hand the treatment at moderate temperatures of mixtures of oxides leads to cation disordered materials as in Sr_2FeMoO_5N.[12]

Here we show that the topochemical ammonolysis of highly ordered Sr_2FeWO_6 at moderate temperatures and using high NH_3 flow rates produces new $Sr_2FeWO_{6-x}N_x$ oxynitrides with nitrogen contents up to x=1.0, keeping the cationic order of the starting double perovskite oxide. The introduction of nitride induces the oxidation of Fe^{2+} to Fe^{3+} and decreases the Néel temperature to 13 K for Sr_2FeWO_5N which is the first 1:1 Fe^{3+}:W^{6+} double perovskite.

$Sr_2FeWO_{6-x}N_x$ perovskites were prepared by heating Sr_2FeWO_6 under NH_3 gas at flow rates between 100 and 1000 cm^3/min, temperatures between 600 and 660 °C and treatment times between 6 and 20 hours. Highly ordered Sr_2FeWO_6 was prepared using the citrate sol-gel method,[15] which involves the formation of a 1:1 mixture of $SrWO_4$ and $SrFeO_{3-x}$ by treatment in air at 800 °C of the resins as intermediate step. This mixture was subjected to a final treatment in Ar/H_2 (95 %/5 % V:V) during 6 h at 1000 °C to obtain the double perovskite. The nitrogen contents were tuned by changing the temperature, time and flow rate of NH_3 in the ammonolysis reactions. High nitrogen contents can be achieved by using high flow rates and moderate temperatures. Temperatures above 660 °C or the use of long treatment times induce, however, the decomposition of the double perovskite

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Electronic Supplementary Information (ESI) available: Experimental details, Rietveld refinement information of Sr_2FeWO_5N and $Sr_2FeWO_{5.8}O_{0.2}$. Electron diffraction patterns and magnetic structure of Sr_2FeWO_5N and Mössbauer parameters of $Sr_2FeWO_{6-x}N_x$ samples. See DOI: 10.1039/x0xx00000x

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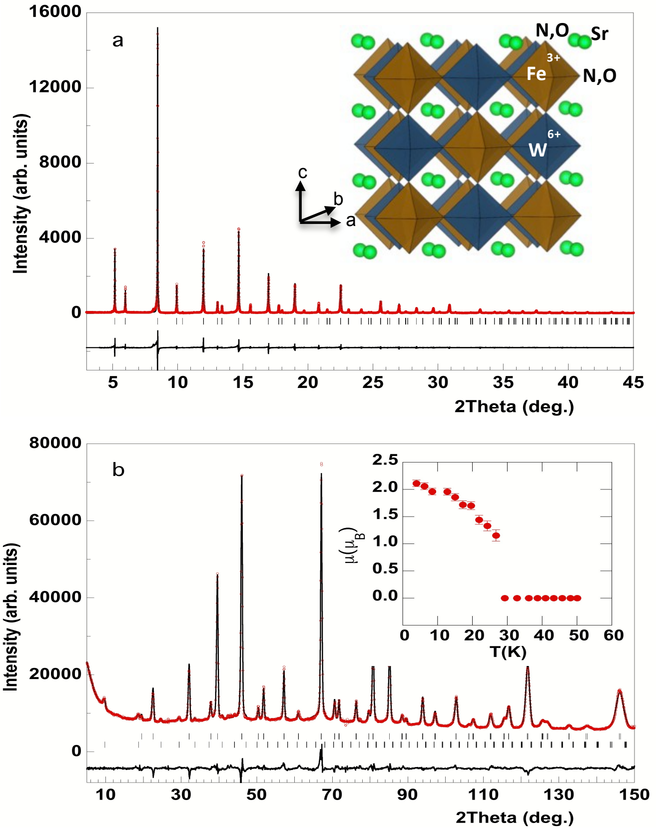

Fig. 1. Rietveld fits to a) synchrotron X-ray powder diffraction pattern at room temperature (λ=0.41269 Å) and b) neutron powder diffraction pattern at 1.8 K (λ=1.54 Å) for Sr_2FeWO_5N in space group I4/m. In b) the upper and lower ticks represent the positions of the nuclear and magnetic reflections respectively. The inset in a) shows the structural model of Sr_2FeWO_5N and in b) it shows temperature variations of the Fe moments.

with formation of Sr_3WO_6. The oxynitrides have been characterized by chemical analysis, electron diffraction, laboratory and synchrotron X-ray and neutron diffraction, Mössbauer spectroscopy and magnetisation measurements. Experimental details are provided in the supplementary information.

The analysed nitrogen contents were between 0.13(2) and 1.03(2) the latter corresponding to the compound Sr_2FeWO_5N that was obtained at 660 °C under ammonia flow rate of 1000 cm^3/min. Quantitative EDS analyses of individual particles confirmed the cationic ratio Sr:Fe:W 2:1:1 and indicated that the samples are compositionally homogeneous. The Rietveld refinement of synchrotron X-ray diffraction data of Sr_2FeWO_6 in the $\sqrt{2}a_p x \sqrt{2}a_p x 2a_p$ cell (a_p= cubic perovskite subcell parameter) with the monoclinic $P2_1/n$ space group[16] showed Fe/W order in 2d/2b Wyckoff sites of 98.4 % (antisite disorder of 1.6 %). The synchrotron X-ray diffraction patterns at room temperature of $Sr_2FeWO_{6-x}N_x$ samples showed the same superstructure peaks, characteristic of the rock-salt ordered double perovskites (figure 1a) and indexed as 0kl reflections with k =2n+1.[17] In contrast the ammonolysis of a 1:1 mixture of $SrWO_4$ and $SrFeO_{3-x}$ produced cation disordered perovskites. (see experimental details and figure S1)

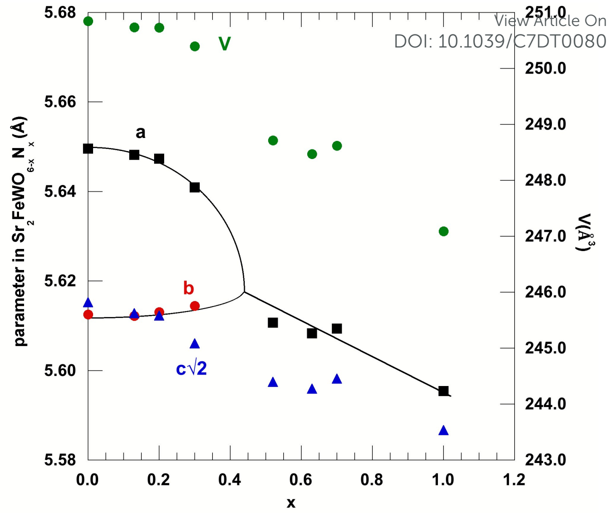

Fig. 2. Reduced cell parameters and volumes as a function of nitrogen content x in $Sr_2FeWO_{6-x}N_x$ perovskites obtained from Rietveld refinement of RT synchrotron X-ray data showing the monoclinic to tetragonal transition at around x=0.4. The solid lines are guides to the eye.

The substitution of oxide by nitride induces the oxidation of Fe^{2+} to Fe^{3+} as a charge compensation mechanism. For nitrogen contents below 0.5 the synchrotron X-ray diffraction data were refined in the same space group as the oxide, $P2_1/n$ (see figure S2 and Table S1). For higher nitrogen contents the symmetry changes to tetragonal I4/m (figures 1 and 2). In all samples no structural transitions were observed in the 10-300 K temperature range. The reconstruction of the reciprocal lattice by electron diffraction of individual crystallites of Sr_2FeWO_5N showed the reflection conditions according to the I4/m space group (see figure S3). The cell parameters of $Sr_2FeWO_{6-x}N_x$ samples decreased with increasing nitrogen content (Figure 2) indicating that the effect of oxidation of Fe^{2+} to Fe^{3+} with ionic radii of 0.78 Å and 0.645 Å respectively outweighs the larger ionic radius of nitride with respect to oxide (r =1.46 (N^{3-}) *vs* 1.38 (O^{2-}) Å for CN=IV).[18] The refined cell parameters from synchrotron diffraction for Sr_2FeWO_5N are a=5.5954(2) and c= 7.9008(1) Å. The refined antisite disorder for this sample was 3.2 %, and below this value for the other samples showing that the cations do not suffer important displacements during the nitriding reaction. The average Fe-(O,N) bond distance observed from synchrotron diffraction in $Sr_2FeWO_{6-x}N_x$ samples decreases with increasing N from 2.095(14) Å for x=0 to 2.02(3) Å for x=1.0, whereas the W-(O,N) bond distance remains constant at c.a. 1.94 Å. According to the ionic radii[18] this result is consistent with the oxidation of Fe^{2+} to Fe^{3+} and the constant oxidation state of +6 for W along the solid solution. The observed tolerance factor calculated as $t_{obs}= \langle A\text{-}X\rangle/\sqrt{2}\langle B\text{-}X\rangle$,[19] where $\langle A\text{-}X\rangle$ and $\langle B\text{-}X\rangle$ are the mean interatomic distances with twelve and six coordination for A and B sites respectively, increases from 0.992 for x=0 to 0.998 for x=1. The transition from monoclinic to tetragonal symmetry is a consequence of the relatively more important reduction in size of B sites with nitriding because of the oxidation of Fe^{2+} to Fe^{3+}, and agrees with the observed correlation between symmetries

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Table 1. Atomic coordinates in tetragonal space group I4/m, cation and anion occupancies and isotropic temperature factors for Sr_2FeWO_5N from the refinement to neutron diffraction data at 50 K using λ= 1.12031 Å. [(a)]

Atom	Wyckoff site	x	y	z	B(Å^2)	Occ. factor
Sr	4c	0.5	0	0	0.55(2)	1
Fe1/ W1	2a	0	0	0	0.57(13)	0.960(16)/0.04
Fe2/W2	2b	0	0	0.5	0.5(2)	0.04/0.96
O1/N1	4e	0	0	0.2578(14)	0.77(8)	0.77(5)/0.23
O2/N2	8h	0.2306(8)	0.2740(9)	0	0.50(4)	0.90(2)/0.10

(a) Estimated standard deviations in parentheses are shown once for each independent variable. Fe/W occupation factors were refined subject to the ideal stoichiometry. Refined cell parameters were a=5.5728(2), c=7.9009(5) Å. Agreement factors: χ^2=3.96; R_{wp}= 2.18; R_{Bragg}=2.20.

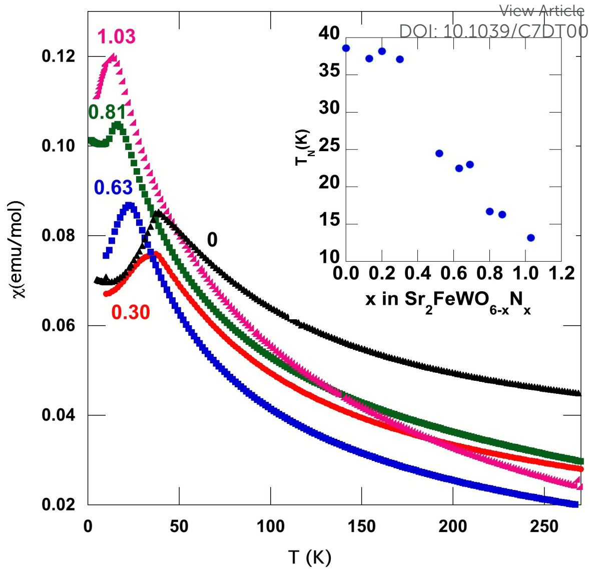

Fig. 3. Magnetic susceptibility data for selected $Sr_2FeWO_{6-x}N_x$ samples with nitrogen contents as shown. Inset shows the dependence of Néel temperature on nitrogen content.

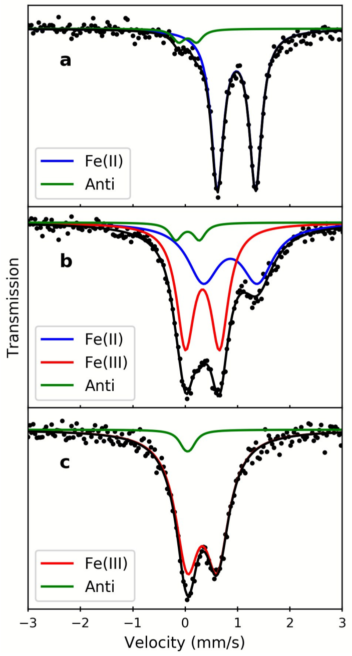

Fig. 4. Mössbauer spectra of a) Sr_2FeWO_6, b) $Sr_2FeWO_{5.37}N_{0.63}$ and c) Sr_2FeWO_5N observed at 295 K showing the contributions of Fe(II), Fe(III) and antisite Fe(III).

and tolerance factors in $A_2B'B''O_6$ perovskites.[20]

Refinement of neutron diffraction data for Sr_2FeWO_5N in I4/m gave O/N occupancies of 90/10 in the equatorial sites 8h and 77/23 in the axial sites 4e. (Figures 1b and S4, and Table 1) The refined nitrogen stoichiometry was 0.86(4). The relative distribution of N in the two sites has a ratio of nearly 1:2 which is similar to that found in $SrTaO_2N$ for the I4/mcm space group which gave 75/25 for O/N in the equatorial sites and 50/50 in the axial sites.[21,22] In $SrTaO_2N$ the anion order lowers the symmetry to Fmmm which splits the equatorial sites into two non equivalent positions with different nitrogen occupancies.[21,23] In Sr_2FeWO_5N the refinements using the space group $P4_2/m$, which in a similar way splits the equatorial sites into two anion sites did not converge, which may be due to the smaller nitrogen content.

The antiferromagnetism of Sr_2FeWO_6 is due to the coupling of localised S=2 moments of high spin Fe^{2+}.[11] Magnetic susceptibility measurements of $Sr_2FeWO_{6-x}N_x$ samples (Figure 3) show that the magnetic ordering temperature decreases with increasing N, from 38 K for x=0 to 13 K for x=1. The suppressing of the magnetic order is induced by hole doping through O^{2-}/N^{3-} substitution as observed for antiferromagnetic Cr^{3+}/Cr^{4+} oxynitrides $LnCrO_{3-x}N_x$ (Ln=lanthanide).[8] The magnetic order of Sr_2FeWO_5N has been investigated by variable temperature neutron powder diffraction. Below 27 K a set of magnetic reflections is observed (Figure 1b) indicating long range antiferromagnetic order. These can be indexed using a (0, ½, ½) propagation vector. The magnetic arrangement is similar to that reported for Sr_2FeWO_6,[16] and can be described as alternating (011) ferromagnetic planes coupled antiferromagnetically (See Figure S5). The magnetic moments are aligned parallel to the c-axis. Although allowed by magnetic symmetry analysis, there are no components along the a- or b-axes and the magnetic space group is P_S-1.[24] The saturated Fe magnetic moment is 2.12(6) μ_B which is below the expected value for Fe^{3+} in high spin configuration indicating that these moments are not fully ordered. The oxynitride $Sr_2FeWO_{5.3}N_{0.70}$ showed a similar magnetic structure but the saturated magnetic moment of Fe was 2.6(1) $\mu_{B,}$ larger than for x=1 according with the suppression of magnetic order with nitride. This tendency agrees with the larger magnetic moment from neutron diffraction data at 10 K reported for Sr_2FeWO_6, 3.86(4) μ_B.[16]

Fe valence states of several oxynitride samples have been investigated using ^{57}Fe Mossbauer spectroscopy measurements (Figures 4 and S6, and Table S2). The spectra fitting was performed by considering contributions from Fe(II) and Fe(III) in one of the B sites, and a small component assigned to antisite Fe(III) occupying the second octahedral position. At room temperature the isomer shifts relative to α-Fe (δ), obtained from the fitted paramagnetic spectrum of

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Sr_2FeWO_6 shown in Figure 4, are δ=1.098(2) mm/s for the main component (93 %) which corresponds to Fe(II), and δ=0.164 mm/s for a weak Fe(III) antisite component (7 %) in agreement with previous reports.[25] The fitting of the spectrum of Sr_2FeWO_5N gives δ=0.443(6) mm/s for the main component (95 %) which is assigned to Fe(III) in 2a Wyckoff sites of the I4/m structure. For samples with intermediate N contents the two contributions assigned to Fe(II) and Fe(III) in the same octahedral site can be identified, with fitted relative intensities according to the analysed O/N ratio, and an additional small antisite Fe(III) component (5 %) as observed in Sr_2FeWO_6.

Double perovskite oxides are a large group of compounds with many possibilities of combinations of A-site and B-site cations and a wide diversity of interesting properties. Perovskite oxynitrides $ABO_{3-x}N_x$ are investigated actively mainly because of their electronic and visible-light photocatalytic properties, but reports on double perovskites $A_2B'B''O_{6-x}N_x$ are restricted to few examples showing either low N contents or high B'/B'' disorder. This study demonstrates that the synthesis of the new cation ordered double perovskite oxynitrides $Sr_2FeWO_{6-x}N_x$ with nitrogen contents up to x=1 proceeds by ammonolysis of Sr_2FeWO_6 through topochemical substitution of oxide by nitride anions with concomitant oxidation of Fe^{2+} to Fe^{3+}. The preparative strategy consists in the use of cation ordered precursors and moderate temperatures to avoid the reduction and the diffusion of the transition metals, together with high NH_3 flow rates, up to 1000 cm^3/min, to ensure high nitrogen contents. The W^{6+}/Fe^{3+} oxynitride Sr_2FeWO_5N is antiferromagnetic but with a lower Néel temperature than the starting oxide. The synthetic method can be applied to other combinations of A, B' and B'' cations opening new perspectives of exploring properties in double perovskite oxynitrides. The combination of two different transition metals that order in the B sites is expected to tune the electronic and photocatalytic properties expanding the applications of this group of compounds.

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Roberta Ceravola, Judith Oró-Solé, Ashley. P. Black, Clemens Ritter, Inés Puente Orench, Ignasi Mata, Elies Molins, Carlos Frontera and Amparo Fuertes

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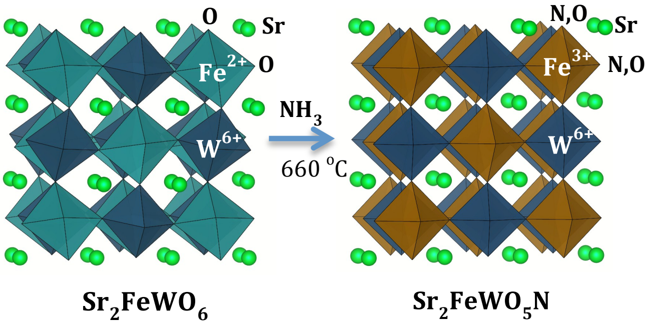
$Sr_2FeWO_{6-x}N_x$ compounds with nitrogen contents up to x=1 are prepared by topochemical ammonolysis at moderate temperatures of B-site cation ordered Sr_2FeWO_6. Sr_2FeWO_5N is antiferromagnetic with T_N=13 K and represents the first double perovskite oxynitride with high cationic order and nitrogen content.



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