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Coupled anion and cation ordering in $Sr_3RFe_4O_{10.5}$ (R=Y, Ho, Dy) anion-deficient perovskites

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1. Introduction

Anion-deficient perovskite-based ferrites demonstrate rich crvstal chemistry and diverse physical properties. The wide range of oxygen non-stoichiometry associated with the variable Fe²⁺-Fe⁴⁺ oxidation state, the ability of iron to adopt octahedral, tetrahedral, distorted five-fold (trigonal bipyramidal of tetragonal pyramidal), and even square-planar coordination creates a variety of structures with different ordering patterns of oxygen atoms and anion vacancies. The simplest ordering pattern arises when all oxygen atoms are removed from the perovskite AO layers, leaving the BO₂ layers intact, as in the "infinite-layer" AFeO₂ (A=Ca, Sr) structures [1,2]. Layered ordering of the oxygen vacancies is preserved at higher oxygen content in the A_2 Fe₂O₅ (A=Ca, Sr) brownmillerites [3-9]. They consist of layers of FeO₆ octahedra interleaving with layers of the FeO₄ tetrahedra and demonstrate a variety of polytypes because of the configurational flexibility of the tetrahedral layers [10,11]. A further increase in oxygen content is obtained either by increasing the amount of the octahedral layers ($LaA_2Fe_3O_8$, A=Ca, Sr

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ABSTRACT

The Sr₃*R*Fe₄O_{10.5} (*R*=Y, Ho, Dy) anion-deficient perovskites were prepared using a solid-state reaction in evacuated sealed silica tubes. Transmission electron microscopy and ⁵⁷Fe Mössbauer spectroscopy evidenced a complete *A*-cations and oxygen vacancies ordering. The structure model was further refined by *ab initio* structure relaxation, based on density functional theory calculations. The compounds crystallize in a tetragonal $a \approx 2\sqrt{2}a_p \approx 11.3$ Å, $c \approx 4c_p \approx 16$ Å unit cell (a_p : parameter of the perovskite subcell) with the *P*4₂/*mnm* space group. Oxygen vacancies reside in the (FeO_{5/4} $\square_{3/4}$) layers, comprising corner-sharing FeO₄ tetrahedra and FeO₅ tetragonal pyramids, which are sandwiched between the layers of the FeO₆ octahedra. Smaller *R* atoms occupy the 9-fold coordinated position, whereas the 10-fold coordinated positions are occupied by larger Sr atoms. The Fe sublattice is ordered aniferromagnetically up to at least 500 K, while the rare-earth sublattice remains disordered down to 2 K.

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[12,13]) or by replacing the FeO₄ tetrahedra by FeO₅ tetragonal pyramids, which form ordered arrangements together with the FeO₆ octahedra in Sr₄Fe₄O₁₁ and Sr₈Fe₈O₂₃ [9]. Completely different situation is realized in the anion-deficient perovskite-based ferrites with the lone pair *A*-cation (Pb²⁺). Point oxygen vacancies are eliminated from the structure of such materials by periodically spaced crystallographic shear planes [14–16].

The ordering of oxygen vacancies can be stabilized by the presence of ordered *A* cations with different sizes, as in YBaFe₂O₅ and YBa₂Fe₃O₈. Here, oxygen atoms are removed from a part of the AO layers, thus transforming the neighboring FeO₆ octahedra into the FeO₅ tetragonal pyramids [17–19]. The smaller Y³⁺ cations (r=1.015 Å, coordination number CN=8) reside in the anion-deficient layers and are 8-fold coordinated by the oxygen atoms, whereas the larger Ba²⁺ cations (r=1.60 Å) have CN=12 in the complete (AO) layers. Coupled oxygen vacancy and partial *A*-cation ordering is also observed in Ca₂Ba₂Nd₂Fe₆O_{15.6} compound, representing an original intergrowth of the brownmillerite and YBa₂Fe₃O₈-type structures [20].

The different anion-deficient perovskites host versatile physical properties. Anion disorder leads to high oxygen conductivity and supports potential applications in solid-oxide fuel cells [21]. The peculiar layered structures of the $AFeO_2$ compounds induce an unusual orbital state of Fe^{2+} [1,2,22] and a spin-state transition under

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pressure [23]. Recent studies explored the thermoelectric properties of $Ca_2Fe_2O_5$ and evidence a reduced thermal conductivity, compared to the ideal $CaFeO_3$ perovskite that lacks anion vacancies [24]. All these findings motivate the search for new Fe-based anion-deficient perovskites.

Our study was guided by a similarity in anion-vacancy ordering patterns of ferrites and cobaltites (compare the Fe- and Co-based $A_2B_2O_5$ brownmillerites or the anion-deficient $AA'B_2O_5$ (A, A' are the cations of different size) perovskites) [25,26]. An original aniondeficient perovskite structure was reported for cobaltites $Sr_{4-x}R_xCo_4O_{10.5+\delta}$ with R=La, Y, Sm-Yb, $0.4 \le x \le 1.33$, and - $0.02 < \delta < 0.74$ (the cation homogeneity range and the oxygen content vary depending on the *R*-type and might also depend on synthesis conditions, causing the discrepancy between published data) [27-29]. The idealized structure of these compounds with the Sr₄RCo₄O_{10.5} composition corresponds to the layer sequence—CoO₂- $AO-CoO_{5/4} \square_{3/4} - AO-CoO_2 - [30-32]$. The anion vacancies are partially ordered in the $(CoO_{5/4}\square_{3/4})$ layers, giving rise to formally five-fold coordinated Co atoms. However, one equatorial oxygen position is only 25% occupied, resulting locally in CoO₄ tetrahedra and CoO₅ distorted tetragonal pyramids in a 1:1 ratio. This structure is realized in the frame of a tetragonal $2a_p \times 2a_p \times 4a_p$ supercell $(a_p$ —a parameter of the perovskite subcell) and the *I*4/*mmm* space group, but further ordering and structural distortions resulting in the unit cell expansion and symmetry lowering are also reported [33,34]. The anion ordering is usually coupled with the ordering of the Sr and R cations: the partially occupied oxygen site is adjacent to the R cations, thus their coordination number is decreased. This coupling seems to be an essential prerequisite for the ordering, although anion ordering can exist even with a random placement of the A cations, as in the case of R=La with similar sizes of Sr^{2+} (r=1.32 Å, CN=10) and La^{3+} (r=1.28 Å, CN=10) [29].

An ordered pattern of anion vacancies, similar to that in the $Sr_{4-x}R_xCo_4O_{10.5+\delta}$ solid solutions, was also observed at partial replacement of Co by Ga or Fe, or even in the completely Co-free $Sr_{2.93}Y_{1.07}Mn_{2.67}Ga_{1.33}O_{10.53}$ compound [35,36]. However, up to now attempts to prepare purely iron-based anion-deficient analogs of the $Sr_4RCo_4O_{10.5}$ phases were unsuccessful. A replacement of Co with Fe in the $Sr_3YCo_{4-x}Fe_xO_{10.5+\delta}$ solid solution allows to maintain the anion–vacancy ordering only up to x=2.5 and yields polyphasic samples for x > 3.5 [35]. In the present study, we avoid this limitation by using a different preparation method and report on the crystal structure and magnetic properties of $Sr_3RFe_4O_{10.5}$ compounds with R=Y, Ho, and Dy. In contrast to cobaltites, the $Sr_3RFe_4O_{10.5}$ ferrites show anion and cation ordering at room temperature.

2. Experimental

The Sr₃*R*Fe₄O_{10.5} (*R*=Y, Ho, Dy) samples were prepared using a solid-state reaction in evacuated sealed silica tubes. SrO, Fe₂O₃, and R_2O_3 (*R*=Y, Ho, Dy) were used as the starting materials. SrO was prepared by a decomposition of SrCO₃ at 900 °C in a dynamic vacuum of 10^{-3} mbar and further handled in an Ar-filled glove box. The starting materials were mixed according to the required cation ratio, placed into alumina crucibles and then into silica tubes. The tubes were evacuated to a residual pressure of 10^{-2} mbar and sealed. The samples were annealed at 1000 °C for 36 h. After furnace cooling, the tubes were opened, the samples were reground, pressed into pellets, sealed, and annealed again at 1100 °C for 48 h. Finally the samples were furnace cooled. Some samples were additionally annealed at 1150 °C for 24 h and then cooled to room temperature with a rate of 3 °C/h.

The oxygen content was analyzed by the carrier-gas-hotextraction technique using a TCH600 LEKO instrument and He as the carrier gas. The analysis yielded 20.2 ± 0.2 wt% of oxygen, which corresponds to a Sr₃RFe₄O_{10.3 ± 0.1} composition. This formula is close to Sr₃RFe₄O_{10.5} with all iron atoms having the oxidation state +3. Since Mössbauer spectroscopy confirms the oxidation state of +3, we further refer to the ideal Sr₃RFe₄O_{10.5} composition.

Phase analysis and cell parameter determination were performed using X-ray powder diffraction (XRPD) with a Huber G670 Guinier diffractometer (Cu $K\alpha_1$ -radiation, image plate detector).

Electron diffraction (ED) and high-resolution transmission electron microscopy (HRTEM) investigations were performed on crushed samples deposited on holey carbon grids. ED patterns were obtained using a Philips CM20 microscope, while HRTEM experiments were performed using a JEOL 4000EX microscope. HRTEM image simulations were made using the JEMS software. Energy-dispersive X-ray analysis was performed with a Philips CM20 microscope equipped with an Oxford Instruments attachment. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were recorded on a Tecnai G2 microscope. HAADF-STEM image simulations were made using the QSTEM software [37].

Mössbauer spectroscopy (⁵⁷Fe) was performed in transmission mode using a constant acceleration Mössbauer spectrometer coupled with a 1024 multichannel analyzer. A ⁵⁷Co/Rh γ -rays source was used for the experiments. The velocity scale was calibrated relative to α -Fe. All isomer shift values (δ) are referred to α -Fe. All experimental data were resolved in sets, with Lorenzian lineshapes using an iterative least square fitting program.

The magnetic susceptibility was measured with a Quantum Design MPMS SQUID magnetometer in the field range 0.1-5 T and in the temperature range 2-750 K. For measurements above room temperature, the powder sample was placed into a sealed quartz tube filled with He.

For ab initio structure relaxation, we chose the Sr₃YFe₄O_{10.5} compound to avoid the treatment of the partially filled and strongly correlated 4f shells of Dy and Ho. The relaxation was based on density functional theory (DFT) band structure calculations in the VASP code [38,39] with the projected-augmented-wave basis set (plane wave energy cutoff 400 eV) [40,41] and the generalized gradient approximation (GGA) for the exchange-correlation potential [42]. The Brillouin zone was sampled by 16 *k*-points. We performed both the spin-unpolarized (GGA) and the spin-polarized (GGA+U) calculations, the latter including the mean-field correction for correlation effects in the Fe 3*d* shell (the GGA+*U* input parameters U=5 eV and J=1 eV, according to previous studies [43]). Since the Fe–O–Fe angles are close to 180° and the experimental data evidence antiferromagnetic (AFM) ordering in Sr₃RFe₄O_{10.5}, a simple AFM ground state with antiparallel spins on neighboring Fe atoms was assumed. The energy spectrum of Sr₃YFe₄O_{10.5} is typical for Fe³⁺ oxides, with valence bands formed by Fe 3d and O 2p states. GGA leads to a metallic spectrum due to an underestimate of the correlation effects, while GGA+Urestores the insulating ground state (energy gap $E_g = 1.8$ eV, consistent with the red-brownish color of the samples). The magnetic moment on the Fe sites is 4.0–4.3 $\mu_{\rm B}$, in agreement with experimental estimates for other Fe³⁺ anion-deficient perovskites [19]. During the relaxation, the atom positions were varied, while the unit cell parameters were fixed at the experimental values. Residual forces in the relaxed structures are below 0.01 eV/Å.

3. Results

3.1. Preliminary investigation

Typical XRPD patterns of the $Sr_3RFe_4O_{10.5}$ (R=Y, Ho, Dy) samples are shown in Fig. 1. They can be indexed in a primitive cubic unit cell with the parameters given in Table 1. The lattice



Fig. 1. Le Bail fit of the X-ray powder diffraction patterns of $Sr_3RFe_4O_{10.5}$ (R=Y, Ho, Dy). The ticks mark the positions of the cubic perovskite subcell reflections.

Table 1	
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Perovskite subcell parameters for $Sr_3RFe_4O_{10.5}$ (R=Y, Ho, Dy).

Sample composition	Ionic radius of R (Å)	a (Å)
Sr ₃ YFe ₄ O _{10.5}	1.155	3.8850(7)
Sr ₃ HoFe ₄ O _{10.5}	1.16	3.8856(5)
Sr ₃ DyFe ₄ O _{10.5}	1.17	3.8871(6)

parameters and the intensity distribution of the reflections on the XRPD pattern reflect that all compounds adopt the perovskitebased structure. The lattice parameter decreases with decreasing ionic radius of the *R* cation. Superstructure reflections and splitting or broadening of the basic perovskite reflections, which could indicate a possible symmetry reduction or an increase in the unit cell volume, were not observed.

EDX analysis demonstrated a Sr:R:Fe atomic ratio close to the nominal 3:1:4 one (Sr:R:Fe=2.9(1):1.17(9):3.9(1) for R=Y: 3.0(1):1.0(1):3.9(1) for R=Ho; 2.95(5):1.17(6):3.87(7) for R=Dy). The Mössbauer spectra of Sr₃DyFe₄O_{10.5} revealed that the compound is in a magnetically ordered state at room temperature. In order to better resolve the signals from inequivalent Fe atoms, the spectrum was measured at T=78 K (Fig. 2). The spectrum consists of three sets of Zeeman sextets with different hyperfine parameters, which were attributed to three distinct atomic positions Fe(1), Fe(2), and Fe(3). The observed isomer shifts IS=0.26-0.43 mm/s correspond to Fe³⁺ cations exclusively (Table 2). According to the isomer shift values, the Fe(1) atoms adopt an octahedral oxygen environment, whereas tetrahedral oxygen coordination is realized for the Fe(3) atoms. The isomer shift for the Fe(2) atoms is in between the isomer shifts of Fe(1) and Fe(3), indicating that the Fe(2) atom is in a five-fold coordination. The observed Fe(1), Fe(2), and Fe(3) sextet areas correspond to the \sim 2:1:1 ratio of the octahedrally, five-fold, and tetrahedrally coordinated Fe atoms.

We conclude that the $Sr_3RFe_4O_{10.5}$ (R=Y, Ho, Dy) compounds adopt an anion-deficient perovskite structure. The presence of the Fe atoms in three distinct coordinations points to an ordered arrangement of the oxygen atoms and anion vacancies, as further verified by electron diffraction.

3.2. Electron diffraction and structure model

All the Sr₃*R*Fe₄O_{10.5} (*R*=Y, Ho, Dy) compounds demonstrate similar ED patterns (Fig. 3). The brighter reflections on the ED patterns belong to the primitive cubic perovskite structure with cell parameter a_p . Besides these subcell reflections, numerous weaker superstructure reflections are present. The most frequently observed pattern along the cubic axis of the perovskite subcell is shown in Fig. 3a. The reflection positions on this pattern match well with a tetragonal symmetry. However, the intensity distribution does not demonstrate four-fold



Fig. 2. The 57 Fe Mössbauer spectrum of Sr₃DyFe₄O_{10.5} at T=78 K.

Table 2

The ^{57}Fe Mössbauer hyperfine parameters of Sr₃DyFe₄O_{10.5}: *I*, relative area; IS, isomer shift relative to α -Fe; Γ , line-width.

	Fe(1)	Fe(2)	Fe(3)
I (%) (± 1)	53	25	22
IS (mm/s) (± 0.02)	0.43	0.39	0.26
Γ (mm/s) (± 0.02)	0.72	0.50	0.77



Fig. 3. Electron diffraction patterns of $Sr_3DyFe_4O_{10.5}$ taken from a twinned region (a) and single domain regions (b–f). The indexation is performed on a tetragonal $2\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$ supercell.

symmetry. A closer inspection of different areas of the crystals in the $\langle 100 \rangle_p$ orientations revealed that they are heavily twinned and the ED pattern of Fig. 3a is a superposition of the ED patterns in Fig. 3b, c and its 90°-rotated counterpart. Single-domain ED patterns are represented in Fig. 3b–f. They can be completely indexed on a tetragonal unit cell with lattice parameters $a \approx 2\sqrt{2}a_p \approx 11.3$ Å, $c \approx 4a_p \approx 16$ Å. The absence of any reflection splitting on the ED patterns from twinned regions, as well as the absence of the splitting and broadening of reflections on the XRPD patterns, indicates that the tetragonal strain in the Sr₃*R*Fe₄O_{10.5} (*R*=Y, Ho, Dy) structures is negligibly small. The observed reflection conditions *hOl*: *h*+*l*=2*n*, 0*kl*: *k*+*l*=2*n* suggest the $P4_2/mnm$ space group or its subgroups $P\overline{4}$ n2 and $P4_2nm$. The forbidden h00: $h \neq 2n$, 0k0: $k \neq 2n$ and 00l: $l \neq 2n$ reflections on the [001], [110] and [101] ED patterns are caused by multiple diffraction.

The lack of superstructure reflections on the XRPD patterns is likely related to the small size of the twinned domains that makes the structure determination from XRPD data essentially impossible. To construct a structural model, the results of electron diffraction, electron microscopy, and Mössbauer spectroscopy were taken into account. The model was further refined via DFT-based *ab initio* structure relaxation. Our proposed model stems from the following experimental observations:

- unit cell parameters and space symmetry determined from electron diffraction;
- the Sr₃RFe₄O_{10.5} composition, confirmed by EDX analysis, chemical analysis and Mössbauer spectroscopy. This composition implies that all Fe atoms are in the oxidation state +3;
- three crystallographically different positions of Fe atoms with coordination numbers 6, 5, and 4 are present in a 2:1:1 ratio.

Although our experimental data do not allow us to exclude partial cation and oxygen ordering, we have constructed the structural model assuming a complete ordering of oxygen atoms and vacancies, as well as of the Sr and *R* cations. The most symmetric $P4_2/mnm$ space group was chosen, and the atomic positions in the tetragonal supercell were calculated from the atomic positions in the perovskite structure using the $\mathbf{a} = 2\mathbf{a}_p - 2\mathbf{b}_p$, $\mathbf{b} = 2\mathbf{a}_p + 2\mathbf{b}_p$, $\mathbf{c} = 4\mathbf{c}_p$ relation between the subcell and the supercell. The cation composition, the oxygen content, and the unit cell parameters of the Sr₃RFe₄O_{10.5} compounds are similar to those of their Co-based analogs ($a_{\text{Fe}} = \sqrt{2a_{\text{Co}}}$, $c_{\text{Fe}} = c_{\text{Co}}$), thus pointing to a similarity between these crystal structures.

The Sr₃*R*Fe₄O_{10.5} structure can be represented by an ordered alternation of perovskite-type layers along the c-axis of the tetragonal supercell: -FeO_{5/4} -AO-FeO₂-AO-FeO_{5/4} -_{3/4}-(A=Sr, R). The Fe cations in the (FeO₂) layers adopt an octahedral oxygen coordination. There are two (FeO_{5/4 \square 3/4}) layers per unit cell, symmetrically related by the 42 screw axis. The Fe atoms in the (FeO_{5/4 \square 3/4}) layers reside in two 8-fold positions (0,1/4,0) and (1/2, 1/4, 0), resulting in four Fe atoms of every position per one (FeO_{5/4 $\square_{3/4}$}) layer. For the oxygen atoms in the (FeO_{5/4 $\square_{3/4}$}) layers, four 4-fold and two 8-fold positions are available, providing 16 oxygen positions per single (FeO_{5/4 \square 3/4}) layer. Six of these 16 positions should be vacant, in agreement with the (Fe_8O_{10}) (=8×(FeO_{5/4}\square_{3/4})) layer composition. In order to get such composition of the (FeO_{5/4} $\square_{3/4}$) with a complete ordering of the oxygen atoms and vacancies, either three out of four 4-fold positions or one 4-fold and one 8-fold position should be vacant. Only the last possibility creates tetrahedral coordination for half of the Fe atoms in the (FeO_{5/4} $\square_{3/4}$) layer and tetragonal pyramidal coordination for another half of the Fe atoms in this layer. This ordering pattern of oxygen atoms and vacancies results in a 2:1:1 ratio of the Fe atoms in octahedral (CN=6), tetragonal-pyramid (CN=5), and tetrahedral (CN=4) coordination, in agreement with the results of the Mössbauer spectroscopy.

The anion ordering modifies the coordination environment for the A cations. In the framework of this model, the A cations can be placed at one 8-fold and one 4-fold position with CN=12, one 8fold and one 4-fold position with CN=10, and one 8-fold position with CN=9. Continuing the analogy with the Co-based phases, the smaller *R* atoms can be placed into the 8-fold position with the lowest coordination number, whereas other positions are occupied by larger Sr cations. The complete model of the ordering in the Sr₃RFe₄O_{10.5} anion-deficient perovskites is shown in Fig. 4. The atomic coordinates are given in Table S1 of the Supplementary data. At this point, the atomic positions are derived from the parent perovskite structure and do not take into account atomic displacements, which necessarily occur in order to optimize the coordination polyhedra and interatomic distances and relieve the strain, imposed by the ordered arrangement of the anion vacancies.

3.3. HAADF-STEM and HRTEM observations

The proposed model of the anion and cation ordering in $Sr_3RFe_4O_{10.5}$ was confirmed by HAADF-STEM and HRTEM observations. The *A*-cation ordering is clearly observed in the [001]



Fig. 4. The structure model of $Sr_3RFe_4O_{10.5}$ (R=Y, Ho, Dy). The FeO₆ octahedra, FeO₅ tetragonal pyramids and FeO₄ tetrahedra are light blue, green and brown, respectively. The Sr and R cations are shown as large yellow and blue spheres. The oxygen atoms at the corners of polyhedra are marked as small blue spheres. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

HAADF-STEM image of Sr₃DyFe₄O_{10.5} (Fig. 5). In the HAADF-STEM image, the contrast has a relation to the average atomic number of an atomic column as $\sim Z^n$ (n=1-2). Thus, the most prominent dots on the image correspond to the projections of the A-cation columns, which form a square pattern, and each square is centered with a weaker dot corresponding to the FeO column. The pure oxygen columns are not visible due to the low atomic number of oxygen. The brightness of the A-cation dots is not uniform: the brighter dots, corresponding to the mixed Sr (Z=38) and Dy (Z=66) columns, and the less bright dots of pure Sr columns alternate, forming a chess-board pattern, consistent with the proposed structure model. The ordered alternation of the Sr and (Sr,Dy) columns is clearly seen from the intensity plot along the row of the A-cation dots (Fig. 5). The [001] HAADF-STEM image, simulated using the proposed structure model, is in excellent agreement with the experimental one (Fig. 5).

As suggested by the ED data, the HRTEM images along the $\langle 100 \rangle_p$ direction show several twinned regions (Fig. 6). The Fourier transforms taken from the left and right part of the image in Fig. 6 show domains in the [001] and [110] orientation; the domain boundary is not well defined though. The major type of the twinning in Sr₃*R*Fe₄O_{10.5} is a 90° rotation twin that aligns the *c*-axis of the tetragonal supercell along the three $\langle 100 \rangle_p$ axes, symmetrically equivalent in the parent perovskite structure.

The [001] and [110] HRTEM images of $Sr_3DyFe_4O_{10.5}$ are shown in Figs. 7 and 8. The Fourier transforms confirm that the images refer to single domains in the [001] and [110] orientation, respectively. The bright dots in the [001] HRTEM image correspond to projections of the *A*-cation and FeO columns. The tetragonal supercell is centered with four brighter dots marking the projections of the mixed (Sr,Dy) columns, whereas the dots of pure Sr columns appear less bright. The simulated [001] HRTEM image at a focus value f = -450 Å and a thickness t = 48 Å is in agreement with the experimental contrast. The [110] HRTEM image was taken at imaging conditions where the bright dots



Fig. 5. [001] HAADF-STEM image of $Sr_3DyFe_4O_{10.5}$. The plot below the image is the intensity profile along the *A*-cation columns as marked with the white rectangle on the image. The simulated image is shown as inset.



Fig. 6. HRTEM image of a twinned area in $Sr_3DyFe_4O_{10.5}$. The left and right parts of the image correspond to the [001] and [110] orientation, respectively. The Fourier transforms from both domains are shown as insets.

correspond to regions of low projected potential (columns of oxygen atoms and/or anion vacancies). In this projection, the oxygen-deficient columns, consisting of oxygen vacancies only or of vacancies and oxygens in a 50:50 ratio, alternate with the vacancy-free oxygen columns. According to the simulated [110] HRTEM image (f= -800 Å, t=32 Å), the ordered arrangement of the oxygen-deficient columns is visible on the image as a pattern of less bright dots surrounded by a darker gray halo.



Fig. 7. [001] HRTEM image of Sr₃DyFe₄O_{10.5}. The Fourier transform is shown as inset at the left bottom corner. The perovskite subcell and the tetragonal $2\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$ supercell are marked with white small and large rectangles, respectively. The simulated HRTEM image (f= -450 Å, t=48 Å) is superimposed and outlined with a white line.



Fig. 8. [110] HRTEM image of Sr₃DyFe₄O_{10.5}. The Fourier transform is added in the bottom left corner. The simulated HRTEM image (f=-800 Å, t=32 Å) is superimposed and outlined by a white line.

The superstructure induced by the anion and cation ordering is clearly visible on the [101] HRTEM image of $Sr_3DyFe_4O_{10.5}$, where dots of different brightness are grouped in rectangles forming a chess-board pattern (Fig. 9). Here the structure is viewed along the close-packed perovskite layers which are parallel to the *b*-axis of the tetragonal supercell. The Sr and Dy atoms are arranged into separated columns in this structure projection. The bright dots correspond to projections of the columns of oxygen atoms which are at the corners of the FeO₆ octahedra. The difference in brightness arises from different surroundings of these oxygen atoms by *A* cations: the dots of the oxygen columns close to the



Fig. 9. [101] HRTEM image of Sr₃DyFe₄O_{10.5}. The simulated HRTEM image (f = -600 Å, t = 39 Å) is superimposed and outlined by a white line.

Dy columns are darker than the dots corresponding to oxygen columns positioned next to Sr atoms only. The simulated [101] HRTEM image (f = -600 Å, t = 39 Å) is in excellent agreement with the experimental one.

3.4. Ab initio structure relaxation

To improve the accuracy of the structural model, we performed the relaxation of the atomic positions. The DFT-based relaxation accounts for the chemical nature of the system and for all the bonding interactions. However, it has an inherent shortcoming related to the treatment of correlation effects in the Fe 3d shell. To test the relevance of such effects, we performed the relaxation within two different approaches: GGA (a nearly free-electron approximation, spin-unpolarized calculation) and GGA+U (meanfield correction for the correlation effects, spin-polarized calculation). The results are collected in the Supporting information, Table S1. Both approaches modify the atomic positions, compared to the initial model. In particular, we find a remarkable tilting of the FeO₆ octahedra (Fig. 10) that leads to several short Y–O bonds (2.35–2.45 Å). The Sr–O distances exceed 2.5 Å, in agreement with the larger size of the Sr cation (Table 3). The tilting of the octahedra modifies the local environment of the 12-fold coordinated Sr(1) and Sr(4) positions. In the relaxed structure, two Sr-O distances exceed 3.5 Å, and the CN is effectively reduced to 10 (Table 3). Despite the different treatment of the Fe 3d shell, GGA and GGA+U lead to a similar oxygen coordination of the iron positions, with slight differences in the Fe-O bond lengths. GGA underestimates the Coulomb repulsion on the Fe site and, consequently, overbonds the iron atoms, so that the GGA+Urelaxed structure looks more realistic. The interatomic distances for the GGA+U-relaxed structure are listed in Table 3.

3.5. Magnetic properties

Magnetic measurements were performed for $Sr_3RFe_4O_{10.5}$ compounds with R=Dy and Ho. The susceptibility was measured



Fig. 10. The crystal structure of $Sr_3YFe_4O_{10.5}$ relaxed within GGA+*U*. The FeO₆ octahedra, FeO₅ tetragonal pyramids and FeO₄ tetrahedra are light blue, green and brown, respectively. The Sr and *R* cations are shown as large yellow and blue spheres. The oxygen atoms at the corners of polyhedra are marked as small blue spheres. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

in the 2–750 K temperature range. The measurements above 500 K led to irreversible changes that are likely caused by a slight change in the oxygen content upon heating. In the following, we focus on the data collected below 500 K only.

For both compounds, the susceptibility increases with decreasing temperature (Fig. 11). The data above 50 K were fitted with a modified Curie–Weiss law $\chi = \chi_0 + C/(T+\theta)$, where χ_0 is the temperature-independent contribution, *C* is the Curie constant, and θ is the Curie–Weiss temperature. The fits yielded χ_0 =

Tal	ble	3

Selected interatomic distances (in Å) in the GGA+U optimized structure of Sr₃YFe₄O_{10.5}.

Y-O(2)	2×2.44	Sr(2)–O(2)	2×2.97	Fe(1)–O(1)	1.95
Y-O(4)	2×2.75	Sr(2)-O(3)	2 × 2.83	Fe(1)-O(2)	2×2.01
Y-O(5)	2.70	Sr(2)-O(4)	2×2.63	Fe(1)-O(3)	2.01
Y-O(6)	2.42	Sr(2)-O(4)	2×2.87	Fe(1)-O(6)	2.07
Y-0(7)	2.82	Sr(2)–O(9)	2×2.76	Fe(2)-O(2)	2.04
Y-O(9)	2×2.36	Sr(3)–O(5)	2×2.73	Fe(2)-O(4)	1.99
Sr(1)-O(1)	3.05	Sr(3)-O(7)	2×2.55	Fe(2)-O(4)	2.02
Sr(1)-O(2)	2×3.01	Sr(3)-O(8)	2×2.90	Fe(2)-O(5)	2.02
Sr(1)-O(3)	2×3.06	Sr(3)–O(9)	4 × 3.11	Fe(2)-O(7)	2.02
Sr(1)-O(4)	2×2.60	Sr(4)-O(1)	2×2.76	Fe(2)-O(9)	2.43
Sr(1)-O(5)	2.60	Sr(4)-O(2)	4×2.74	Fe(3)-O(3)	1.93
Sr(1)-O(7)	2.63	Sr(4)–O(5)	2×2.69	Fe(3)-O(8)	1.93
Sr(1)-O(8)	3.10	Sr(4)–O(7)	2×2.96	Fe(3)–O(9)	2 imes 1.88



Fig. 11. Magnetic susceptibility of $Sr_3RFe_4O_{10.5}$ with R=Dy (top) and Ho (bottom). Experimental data, shown with open circles, were measured in an applied field of 0.1 T. Solid lines are fits of the data with the modified Curie–Weiss law.

7.5(1) × 10⁻³ emu/mol, C=14.74(1) emu K/mol, and $\theta=9.8(1)$ K for R=Dy and $\chi_0=7.4(1) \times 10^{-3}$ emu/mol, C=15.04(1) emu K/mol, and $\theta=6.3(1)$ K for R=Ho. The effective moments of 10.86(1) and 10.97(1) μ_B for R=Dy and Ho, respectively, are in reasonable agreement with the expected values of 10.65 and 10.61 μ_B . Thus, the temperature dependence of the magnetic susceptibility can be attributed to the paramagnetic behavior of the rare-earth cations.

According to the results of the Mössbauer spectroscopy, the Fe sublattice is in a magnetically ordered state at room temperature. To find out the type of the magnetic ordering, we measured magnetic susceptibility in different applied fields. At low temperatures, we observed a pronounced suppression of the susceptibility by the applied field, typical for paramagnets. Above 40 K, the susceptibility does not depend on the field. Hence, the ordering in the Fe sublattice is antiferromagnetic and persists up to at least 500 K. The Fe contribution to the magnetic susceptibility is low and can be roughly approximated by the constant χ_0 term.

The smooth temperature dependence of the magnetic susceptibility indicates the lack of a magnetic ordering transition in the 2–500 K temperature range. Positive Curie–Weiss temperatures θ correspond to weak and predominantly antiferromagnetic interactions between the rare-earth atoms. Indeed, the susceptibility shows a negative deviation from the Curie–Weiss law below 20 K, revealing the onset of antiferromagnetic correlations between the magnetic moments on the rare-earth atoms.

4. Discussion

Synthesis by a solid-state reaction at 1100-1150 °C in evacuated sealed silica tubes allowed us to prepare the singlephase $Sr_3RFe_4O_{10.5}$ (R=Y, Dy, Ho) compounds with an ordered arrangement of oxygen atoms and anion vacancies, as well as Sr and *R* cations. This result can be compared with the attempts to partially replace Co by Fe in Sr₃YCo₄O_{10.5}, performed by a solidstate reaction at nearly the same temperature (1100 °C) and higher partial oxygen pressure (in air). Initially, in Sr₃YCo₄O_{10.5} the oxygen vacancies are partially ordered in the $(CoO_{5/4} \square_{3/4})$ layers. This ordering gives rise to a tetragonal $2a_p \times 2a_p \times 4a_p$ superstructure, where one position of the oxygen atom, occupied by 25%, forms a common vertex of two CoO₅ distorted tetragonal pyramids (also considered as being more close to trigonal bipyramids) (Fig. 12a). This type of ordering is maintained in the Sr₃YCo_{4-x}Fe_xO_{10.5+ δ} solid solution only up to x=2.5, and between $3 \le x \le 3.5$ a disordered perovskite structure was observed. The synthesis of the fully substituted $Sr_3YFe_4O_{10.5+\delta}$ yielded a multiphase sample [30]. Suppression of the anion ordering in the Sr₃YCo_{4-x}Fe_xO_{10.5+ δ} solid solution is presumably related to increasing oxygen content because of the thermal treatment in air. Indeed, for the x=2 sample, δ was found to be 0.304 [30]. Synthesis of Sr₃RFe₄O_{10.5} in a sealed silica tube, performed in the present work, prevents the partial oxidation of Fe³⁺ to Fe⁴⁺ and maintains the chemical composition and the ordered structure of the (FeO_{5/4} $\square_{3/4}$) layers.

Partial anion ordering in the anion-deficient layers with the idealized (CoO_{5/4 $\square_{3/4}$}) composition (Fig. 12a) associated with the $2a_{p} \times 2a_{p} \times 4a_{p}$ superstructure was reported for a wide range of $Sr_{4-x}R_xCo_4O_{10.5+\delta}$ compositions [22–24]. The broad homogeneity range of these solid solutions indicates that the ordering in these compounds is intrinsically incomplete. In the frame of the $2a_{\rm p} \times 2a_{\rm p} \times 4a_{\rm p}$ unit cell and the *I*4/*mmm* space group, the occupancy factors are the same for the partially vacant oxygen sites at the trans- and cis-positions with respect to the R cations above and beneath the layer (viewed along [001] axis) (Fig. 12a). An extra ordering was reported to result in either an orthorhombic C-centered $2\sqrt{2}a_p \times 4a_p \times 2\sqrt{2}a_p$ superstructure or in an A-centered monoclinic $2\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$ superstructure. In the C-centered orthorhombic superstructure, the oxygen sites at trans-positions acquire different occupancies (Fig. 12b) [28]. The A-centered monoclinic supercell arises as a result of the order-disorder phase transition redistributing oxygen atoms in such a way that one pair of the oxygen trans-positions becomes completely vacant, and another pair of trans-positions is 50% occupied (Fig. 12c) [29]. The tetragonal $2\sqrt{2}a_{p} \times 2\sqrt{2}a_{p} \times 4a_{p}$ supercell and the $P4_{2}/mnm$ space symmetry of Sr₃RFe₄O_{10.5} provide a possibility for complete ordering of the oxygen atoms. The perovskite (BO₂) layer can be formally considered as a -O-BO-O-BO- sequence of atomic chains



Fig. 12. The anion-vacancy ordering schemes in the $Sr_{4-x}R_xB_4O_{10.5+\delta}$ (*B*=Co, Fe) compounds: (a) the ($CoO_{5/4}$ _{3/4}) layer in the $2a_p \times 2a_p \times 4a_p$ unit cell (outlined with a square). The partially occupied oxygen positions are shown as small open circles. (b) The anion-deficient layer in the *C*-centered $2\sqrt{2}a_p \times 4a_p \times 2\sqrt{2}a_p$ supercell. Only part of the unit cell is shown. The partially occupied oxygen positions with different occupancies are marked with black and open small circles. (c) The anion-deficient layer in the *A*-centered monoclinic $2\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$ supercell. Only part of the unit cell is shown. The partially occupied oxygen positions are marked by small open circles. (d) The (FeO_{5/4} _{3/4}) layer in the tetragonal $2\sqrt{2}a_p \times 4a_p \times 2\sqrt{2}a_p \times 4a_p$ supercell (outlined with a solid square). The dashed square corresponds to the part of the unit cell shown in (a). On all figures the *BO*₅ tetragonal pyramids and *BO*₄ tetrahedra (*B*=Co, Fe) are green and brown, respectively; the Sr and *R* cations are shown as yellow and blue circles. The atomic displacements are neglected for clarity in all structures. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

running along $[100]_p$ and alternating along $[010]_p$. In the Sr₃RFe₄O_{10.5} structure every second O chain is absent and every fourth oxygen position in the BO chain is vacant resulting in the - \Box -FeO_{3/4} \Box _{1/4}-O-FeO_{3/4} \Box _{1/4}- \Box - sequence (Fig. 12d). This ordered arrangement of oxygen atoms and vacancies transforms the infinite net of FeO₆ octahedra into a pattern of blocks consisting of four FeO₄ tetrahedra and four FeO₅ tetragonal pyramids sharing corners with each other. The completely ordered (FeO_{5/4} $\square_{3/4}$) layer does not have a four-fold symmetry, and the overall tetragonal symmetry of the structure is maintained only by the 42 screw axis relating the anion-deficient layers at z=0 and 1/2. Along the *c*-axis, such anion-deficient layers alternate with the layers consisting of corner sharing FeO_6 octahedra (Fig. 4). Thus, the Fe atoms with coordination numbers 6, 5, and 4 are present in the structure in a 2:1:1 ratio. The complete ordering in the anion sublattice is accompanied by an A-cation ordering: the smaller R atoms occupy the positions with CN=9, whereas the positions with CN=10, 12 are occupied by the larger Sr atoms. This ordering pattern is virtually the same as the *A*-cation ordering in nearly stoichiometric $Sr_3RCo_4O_{10.5+\delta}$ compounds.

The magnetic behavior of $Sr_3RFe_4O_{10.5}$ is typical for aniondeficient perovskites containing Fe^{3+} . The dominating couplings in the Fe sublattice arise from the Fe–O–Fe superexchange. Since Fe polyhedra share corners, the Fe–O–Fe angles are close to 180° and lead to strong antiferromagnetic interactions, the antiferromagnetic ground state with antiparallel spins on nearest neighbors, and the magnetic ordering temperatures in the 500–1000 K range [13,19]. Indeed, Mössbauer spectroscopy experiments and magnetic measurements evidenced antiferromagnetic ordering in the Fe sublattice up to at least 500 K. The shortest distance between the *R* cations is about 4.5 Å (along *c*) and may be responsible for the weak antiferromagnetic interactions between the rare-earth cations. However, the separations along *a* and *b* exceed 6.5 Å, thus impeding a three-dimensional (long-range) ordering in the R sublattice. According to our observations, the magnetic moments of the R cations remain disordered down to 2 K.

Despite the complete cation and anion ordering at room temperature, the oxygen atoms in the anion-deficient layers should become mobile at high temperatures, similar to the $Sr_{3+x}R_{1-x}Co_4O_{10.5+\delta}$ cobaltites [34,44]. This motivates further investigation of the $Sr_3RFe_4O_{10.5}$ compounds as potential oxygenion conductors. It may also be interesting to reduce the oxidation state of the iron atoms by removing part of the oxygen atoms and to achieve new low-dimensional structures with a complete cation ordering (similar to [1,2]). Finally, a substitution on the *R* site would explore the role of size effects for the cation and anion ordering in the anion-deficient perovskite-type structures.

In summary, we have prepared and investigated a new family of Fe-containing anion-deficient perovskite-type compounds. At room temperature, these compounds exhibit ordering on the cation and anion positions. Despite the apparent lack of the superstructure reflections in the XRPD data, we were able to deduce the structural model from electron diffraction, electron microscopy and Mössbauer spectroscopy, followed bv a DFT-based structure relaxation. The resulting model shows three different types of Fe coordination (octahedron, tetragonal pyramid and tetrahedron) and typical size effects: the ordering of vacancies and the tilting of polyhedra to achieve a lower coordination number and shorter bonds for the smaller R cations. The Fe sublattice in Sr₃RFe₄O_{10.5} is antiferromagnetically ordered up to at least 500 K, while the rare-earth sublattice exhibits paramagnetic behavior and lacks long-range order down to 2 K.

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2010.09.039.

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