Spin ordering and physical properties of NaPrFeWO₆ and NaSmFeWO₆ with polar double perovskite structure.

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Abstract.

NaPrFeWO₆ and NaSmFeWO₆ have been synthesized as polycrystalline powders by means of a sol-gel route. Both samples adopt a noncentrosymmetric structure derived from the simple perovskite ABO₃ and characterized by a layered ordering of A-site atoms (Na and rare earth) and a rock-salt ordering of B-site atoms (Fe and W) as deduced from x-ray and neutron powder diffraction techniques. Magnetization measurements revealed antiferromagnetic ordering below $T_N \sim 23$ K in both compounds but weak spontaneous magnetization is observed in the hysteresis loops of the samples above and below T_N revealing a parasitic ferromagnetic component that comes from minor ferromagnetic impurities. The magnetic structure of NaPrFeWO₆ is formed by two antiferromagnetic sublattices (rare earth and Fe) that follow the same propagation vector $\mathbf{k} = (\frac{1}{2}, 0, \frac{1}{2})$. The magnetic structure is purely collinear with the moments oriented along the *b*-axis. It presents competitive magnetic interactions and reduced ordered moments at low temperatures. The rare earth moments in the zig-zag chains running along *a* (parallel to the *ab* plane) are ordered following a sequence typical of an E-type arrangement (up-up-down-down). Each Fe²⁺ atom has four nearest Pr³⁺ neighbors and it is coupled antiferromagnetically to three of them and ferromagnetically to the fourth one. Strong neutron absorption from Sm atoms hinders obtaining reliable neutron patterns of NaSmFeWO₆ for Rietveld analysis but the comparison of neutron patterns above and below T_N detected the same magnetic peaks indicating a similar magnetic structure. Dielectric measurements are compatible with a paraelectric system with a strong Maxwell-Wagner contribution from depletion layers and electrical properties are dominated by leakage currents.

Keywords: Polar oxides, doubly ordered perovskites, multiferroics, neutron diffraction, magnetic ordering, depletion layers.

Graphical abstract.

1. Introduction.

Transition metal oxides with the perovskite structure have stimulated a permanent interest in diverse fields because of the wide range of physical properties including superconductivity, magnetoresistance or ferroelectricity [1-3]. The reason is the high versatility of the perovskite structure that admits many possibilities of exotic orderings including arrangements of ions, vacancies and even electron anisotropies such as orbital ordering [4,5]. Focusing on the cationic sublattice, the prototype perovskite ABO_3 is composed of relatively small B cations forming BO_6 octahedra and large A atoms occupying the free space between these octahedra. When the A and/or B positions are occupied by cations with strong differences in size and/or charge, long range ordering of these cations may occur. The bibliography includes many examples of double perovskites $\text{A}_2\text{BB}'\text{O}_6$ with rock salt ordering of an even mixture of B and B' cations [6,7]. Moreover, layered ordering is preferred in $\text{A}'\text{AB}_2\text{O}_6$ compounds for an even mixture of A and A' cations [8,9]. However, the simultaneous ordering in both sites to give $\text{AA}'\text{BB}'\text{O}_6$ compounds is rare and, although it has been little explored, it seems to be observed in a limited combination of atoms [10-14]. Recently, interest in these compounds has increased because they usually adopt a noncentrosymmetric structure with space group $P2_1$ (No. 4) and the compounds with this space group may simultaneously have the following properties: enantiomorphism, optical activity, piezoelectricity and pyroelectricity [15,16]. If we add the presence of magnetic cations these compounds are considered excellent candidates for obtaining new multiferroics. Earlier attempts to prepare NaLnFeWO_6 compounds (Ln=rare earth) by solid state chemistry were unsuccessful [17]. However, the use of soft chemistry methods was effective to prepare NaLaFeWO_6 and NaNdFeWO_6 [18].

The present research has allowed us to increase the family of perovskites $\text{AA}'\text{BB}'\text{O}_6$ with double ordering. We report here the synthesis and characterization of two new members in this family: NaPrFeWO_6 and NaSmFeWO_6 . A modified citrate route was used to prepare them and both samples show long range magnetic ordering at low temperature. Regarding the other two NaLnFeWO_6 synthesized compounds [18] (Ln=La, Nd), we observe a similar magnetic structure following the propagation vector $\mathbf{k}=(\frac{1}{2}, 0, \frac{1}{2})$ and spontaneous magnetization at low temperature. This magnetic contribution is very interesting with a view to enhance the multiferroic properties of these compounds but it presents a problem in the description of the magnetic structure.

It was ascribed to a canting of the magnetic moments yielding a non-collinear magnetic structure. However, symmetry analysis indicates that the ferromagnetic signal is incompatible with the magnetic group (P_{d21}) resulting from the vector $\mathbf{k} = (1/2, 0, 1/2)$, unless there is a multi-K structure due to magnetic frustration and then ferromagnetism would arise from the propagation vector $\mathbf{k}=0$. Competitive magnetic interactions are clearly noticeable in these compounds as the rare earth moments are aligned forming an E-type structure observed in compounds where the nearest-neighbor and next-nearest-neighbor magnetic interactions are of similar intensities [19-21]. Therefore, a careful analysis of the magnetic properties will be conducted in order to clarify the magnetic ground state of these compounds. Furthermore, we show electrical measurements at low temperature in order to disclose the occurrence of spontaneous electrical polarization in this polar structure.

2. Experimental Section.

NaPrFeWO₆ and NaSmFeWO₆ were prepared by a sol-gel method using a modified citrate route. The procedure was as follow: stoichiometric amount of (NH₄)₁₀W₁₂O₄₁ was solved in 60 mL of hot water containing 6 g of citric acid. Thus, stoichiometric amounts of Pr₆O₁₁ (or Sm₂O₃), Na₂CO₃ and FeC₂O₄.2H₂O were added with continuous stirring. In order to complete the solution of all compounds, HNO₃ (65%) is added drop by drop to the solution. Normally, between 4 and 5 mL are enough to achieve a light yellow solution. Then, 3 mL of ethylene-glycol is added to the solution and it is evaporated giving rise to a gel that is dried by heating at 250°C. The resulting powder is heated in a furnace at 600°C during 8 h to remove the organic components and a brown powder is formed. This powder is pressed into pellets and heated at 850°C during 2 h in a reducing flow of H₂/Ar (2/98). The synthesis of other samples with different rare earth atoms (Eu, Gd and Tb) was also tried following the same procedure.

The samples were characterized by powder x-ray diffraction (XRD) with a Rigaku D-Max system using Cu K $\alpha_{1,2}$ wavelengths. Powder neutron diffraction measurements were performed at the high flux reactor of the ILL using the high intensity powder diffractometer D1B ($\lambda=2.52$ Å) with a detector angular range coverage $5^\circ \leq 2\theta \leq 128^\circ$ which is especially suited for magnetic structure determination. Diffraction

patterns were collected between 2 and 50 K. Both, x-ray and neutron diffraction patterns were analyzed by the Rietveld method using the Fullprof program [22]. Magnetic measurements were carried out between 2 and 300 K by using a commercial superconducting quantum interference device (SQUID) magnetometer from Quantum Design. The dielectric measurements were carried out as a function of temperature between 5 and 300 K in a He cryostat employing a homemade coaxial-line inset. Sintered discs with diameter of ~ 8 mm and thickness of ~ 0.9 mm were used. Silver paint was applied to the disc surface for proper electrical contact. The complex dielectric permittivity of the samples was measured using an impedance analyzer (WayneKerr Electronics 6500B), applying excitations of 1 V in a frequency range between 10 Hz and 5 MHz.

Electrical polarization versus electric-field loops measurements were performed on similar disc-shaped pellets using silver paint in sandwich geometry. The sample polarization was recorded using a commercial polarization analyzer (aixACCT Systems Easy Check 300) for frequencies up to 250 Hz using sinusoidal excitation voltages and electric-field amplitudes of 1-8 kV cm⁻¹.

3. Results and discussion.

Fig. 1 compares the x-ray patterns of NaLnFeWO₆ samples with Ln=Pr, Sm, Eu, Gd and Tb. The main peaks are in agreement with the typical ones of a perovskite phase including the characteristic reflections of a layered ordering in the A-site, as (001), and the rock salt ordering in the B-site, as (111). Another feature in the patterns is the occurrence of secondary phases. These are tiny for NaPrFeWO₆ and NaSmFeWO₆ ($\leq 1\%$) and their amounts increase as Ln-size decreases. These results suggest that the stability of the perovskite phase strongly depends on Ln-size and it is smaller for heavy rare earths atoms under synthesis conditions applied. The common impurities were identified as Na₂WO₄ (spinel phase) and NaLnWO₄ (scheelite phase) that are very prominent for the Eu-, Gd- and Tb-based samples. For this reason, this study is focused on NaPrFeWO₆ and NaSmFeWO₆ compounds.

3.1. Crystal structure at room temperature.

Fig. 2 shows the Rietveld refinements of the XRD patterns for NaPrFeWO₆ and NaSmFeWO₆. They were refined in the monoclinic space group $P2_1$, also reported for related compounds [18]. According to previous symmetry analysis, this space group is

adopted by doubly ordered $AA'BB'O_6$ perovskites with tilting distortions of $B(B')O_6$ octahedra according to the $a^-a^-c^+$ tilt system in the Glazer's notation [23]. This implies out-of-phase tilts of equal magnitude about the a - and b -axes, and in-phase tilt around c -axis. A general projection of the crystal structure can be seen in the supplementary information (Fig. S1). Our refinements confirm this space group for both samples. Our attempts to refine antisite defects in A- and B-sites yielded an order of $\sim 97(1)\%$ for the layered ordering (Na/Ln) and $\sim 99(1)\%$ for the rock salt order (Fe/W) suggesting an almost perfect double order in both samples. Tables 1 and 2 show the refined structural parameters of these compounds. Following the lanthanide contraction, the unit cell of NaSmFeWO₆ is smaller than NaPrFeWO₆. However, the volume change is not isotropic and while the bc -plane is contracted in NaSmFeWO₆ respect to NaPrFeWO₆, the a -axis is expanded. Therefore, the lattice parameters sequence is $a \sim b < c/\sqrt{2}$ and $b < a < c/\sqrt{2}$ for Pr- and Sm-based compounds, respectively. FeO₆ and WO₆ octahedra show strong distortions, especially the later. This is due to oxygen shifts toward the Pr-layer in order to stabilize the charge difference between the two A-layers. Our refinements show that W atoms (and also Fe) are displaced from the octahedra center toward Na-layer to stabilize oxygen valences as indicated previously (see Fig. 3). Bond valence sums (BVS) were calculated using the Zachariasen formula [24]. The BVS values obtained reasonably agree with the nominal ones in the NaPrFeWO₆ sample for all atoms indicating their stable environment in this structure. This analysis suggests Fe²⁺ and W⁶⁺ valences for the atoms at the B-sites. However, BVS values move away from ideals in the NaSmFeWO₆ sample indicating structural instabilities which may be at the origin of the difficulty of stabilizing this phase with heavier rare earths. In particular, Fe is strongly over bonded whereas W begins to be under bonded in this structure suggesting that heavy rare earth atoms could disfavor the checkerboard ordering of atoms in the B-sublattice.

In order to gain insights into the possible spontaneous polarization due to the atomic shifts in this polar structure, a symmetry mode analysis [25,26] was performed using the program AMPLIMODES [27]. We have used the refined data at room temperature for NaPrFeWO₆ and NaSmFeWO₆ (tables 1-2) and the parent undistorted structure has the tetragonal $P4/nmm$ symmetry [15]. In the parent structure one can find the layered Na/Pr and rock salt Fe/W orderings without BO₆ octahedra tilts. The modes decomposition relating $P4/nmm$ and $P2_1$ symmetries is composed by 30 individual

modes grouped in 6 irreducible representations (Irrep), namely GM1+, GM2+, GM5+, GM1-, GM2- and GM5-. Rotation of BO₆ octahedra are associate to modes belonging to Irrep GM5+ and GM1- showing global distortions of 1.18 Å (or 1.10) and 0.34 Å (or 0.82), respectively for Pr-(or Sm-)based samples. The abovementioned displacements of Fe and W atoms along z-direction (see Fig. 3) belong to modes of the Irrep GM1+ which has a global distortion of 0.45 Å (or 0.43). Finally, only modes belonging to the Irrep GM5- allow ferroelectric displacements along the unique axis. Its global amplitude is 0.74 Å (or 0.66) and the greatest displacement correspond to apical oxygens (O5 and O6 in tables 1-2) that move in opposite direction to the Pr³⁺ and Na⁺ cations. The smallest shifts along b-axis correspond to Fe²⁺ and W⁶⁺ with similar magnitude. They are moved in the same direction of A-cations. The displacements of the equatorial oxygens along y-direction give rise to mutually cancelling polarizations. Calculation of the theoretical displacive-type ferroelectric polarization [28, 29] yield 25.5 and 21.4 $\mu\text{C cm}^{-2}$ for NaPrFeWO₆ and NaSmFeWO₆, respectively (see Fig. S2 in the supplementary information). These values are in good agreement with previous calculations on NaLaMnWO₆ [15]. Details of the symmetry mode analysis and displacive-type ferroelectric polarization of each atom can be found in the supplementary information.

3.2. Magnetic properties.

Magnetic measurements disclose the presence of a magnetic transition at low temperature for both samples. Figure 4a shows the temperature dependence of dc magnetization under a field of 1 kOe in zero-field-cooled (ZFC) and field-cooled (FC) conditions. These measurements reveal a strong magnetic irreversibility suggesting further competitive interactions. The magnetization curves exhibit clear peaks at $T_N \sim 23$ and $T_N \sim 21$ K for Pr- and Sm-based compounds, respectively. The peaks appear in both ZFC and FC branches at the same temperature. Above T_N , the temperature dependence of paramagnetic susceptibility does not obey the Curie-Weiss law. Deviations from the Curie-Weiss behavior observed in related perovskites are usually ascribed to the anisotropic g-factor and van Vleck susceptibilities [30]. However, these effects are not expected in the present case and the strong magnetic irreversibility seen in Fig. 4a suggests the occurrence of additional magnetic contributions above T_N preventing a normal paramagnetic state of the samples. The ac magnetic susceptibility at different frequencies was measured around T_N for both samples showing the same behavior. Fig. 4b shows the results for NaSmFeWO₆. The magnetic transition is characterized by a

sharp peak in both samples. The peak does not shift with the frequency of the magnetic field. This lack of dynamic behavior discards the formation of a spin glass phase and points out to an antiferromagnetic ordering. Fig. 4c and 4d show the hysteresis loops of both samples below and above T_N . They exhibit spontaneous magnetization followed by a linear increase of the magnetization with increasing the external magnetic field in the whole temperature range tested (5-300 K for Pr-based sample and 5-80 K for the Sm-one). The data at 5 K resemble the results obtained for NaLaWFeO₆ and NaNdWFeO₆ in Ref. 18 suggesting that this is a common behavior in this type of compounds. Unfortunately, Ref.18 did not report $M(H)$ loops above T_N to verify this point. These loops are typical of the addition of a linear contribution, either paramagnetic (PM) above T_N or antiferromagnetic (AFM) below T_N , and of a tiny ferri- or ferromagnetic (FM) contribution which extends to room temperature and can be likely ascribed to magnetic impurities. In order to evaluate the FM signals of both samples, we have fitted the $M(H)$ curves (solid line in Fig. 4c-d) to the formula [31]: $M(H)=a \times \tan^{-1}[(H \pm H_c)/H_c] + \chi H$ (1), and $a = 2M_s/\pi$. The first term in (1) represents a ferromagnetic (FM) component while the linear part of the second term corresponds to the PM or AFM part. In this way, M_s , M_R and H_c stand for saturation magnetization, remanent magnetization and coercive field of the FM signal, respectively while χ refers to the magnetic susceptibility of the PM signal. Table S4 in the supplementary information summarizes the obtained parameters. On comparing the fitted results for both samples at 5 K (see Fig. 4c-d), we note that M_s decreases from $3.7 \times 10^{-3} \mu_B/\text{fu}$ in NaPrFeWO₆ down to $1.4 \times 10^{-3} \mu_B/\text{fu}$ in Sm-based sample whereas H_c increases from 284 Oe in Pr-compound to 925 Oe in the Sm-one. These values indicate a larger number of defects in the Sm-based material anchoring magnetic domains. In the PM region (above 30 K), H_c decreases with decreasing temperature. In both cases, M_R is very small (around $1.8 \times 10^{-2} \mu_B/\text{fu}$) and χ is around $1.5 \times 10^{-5} \mu_B/\text{Oe}$, independently of the rare earth atom. When heating above T_N , the PM signal decreases for both samples reaching values of $2.5 \times 10^{-6} \mu_B/\text{Oe}$ at 300 K for the Pr-based in agreement with the decrease of the PM contribution on warming. However, M_R shows a smaller decrease achieving a value of $3.2 \times 10^{-3} \mu_B/\text{fu}$ at 300 K for the same sample. This suggests a high Curie temperature for the magnetic impurity and, according to the synthesis conditions, segregation of α -Fe particles could be the most likely possibility. The detection of such particles is extremely hard by conventional diffraction techniques (about 0.14% in vol. according to M_s). In summary,

our results agree with an AFM ordering of the main phase with a presence of minor impurity magnetic phase, likely α -Fe, which prevents that these samples obey the Curie-Weiss law at zero field. In order to verify it, ac magnetic susceptibilities using a dc field of 20 kOe (magnetic impurity is saturated according to the hysteresis loops of Fig 4c-d) were measured between 5 and 300 K. The results are shown in the Fig. 5. The plots show the anomaly ascribed to long range AFM order and a linear $\chi^{-1}(T)$ behavior in agreement with the Curie-Weiss law. Both samples show negative Weiss constants consistent with AFM correlations, whose magnitude is close to the experimental T_N . The effective paramagnetic moments are in excellent agreement with the ones expected from the tabulated experimental values [32] of Fe^{2+} ($5.4 \mu_B$), Pr^{3+} ($3.5 \mu_B$) and Sm^{3+} ($1.7 \mu_B$).

3.3. Magnetic ground state.

In order to gain insights into the magnetic properties of these samples, neutron diffraction measurements were collected at low temperature. Because of the strong neutron absorption cross section of ^{150}Sm , neutron data of the Sm-based compound were very poor. However, we could compare neutron patterns above and below T_N detecting two magnetic peaks (see Figure 6) showing the same propagation vector than the one observed in the Pr-based sample. This observation strongly suggests the same magnetic arrangement for both compounds. As the data obtained for the Pr-based sample are of much better quality, the neutron diffraction study was focused on this sample. Figure 6 also shows the neutron thermodiffractograms for NaPrFeWO_6 between 2 and 50 K. Magnetic scattering is noticeable below ~ 22 K with the appearing of new peaks indexed as $(h/2, k, l/2)$ as can be seen in the Fig. 6. This indicates that the magnetic arrangement follows the propagation vector $\mathbf{k}=(1/2, 0, 1/2)$ (A-point of the Brillouin Zone) as reported for related compounds [18]. We have used Isodistort program [33,34] to explore the magnetic irreducible representations for the nuclear cell with $P2_1$ symmetry. The search was limited to the A-point in agreement with the previous propagation vector. The corresponding magnetic space group (MSG) is polar (like its parent supergroup): $\text{Pa}2_1$ (4.10) and the lattice parameters of the magnetic unit cell in the standard setting are derived from the nuclear ones using the lattice vectors: $\mathbf{a}_M=(2, 0, 0)$, $\mathbf{b}_M=(0, 1, 0)$ and $\mathbf{c}_M=(-1, 0, 1)$. Fig. 7 shows the Rietveld refinement and the magnetic structure following this standard setting. The refined lattice parameters for the Pr-based sample are $a_M= 11.0046(8) \text{ \AA}$, $b_M= 5.4971(4) \text{ \AA}$, $c_M= 9.5567(6) \text{ \AA}$ and

$\beta=124.822(4)^\circ$. This unit cell corresponds to the smallest primitive magnetic cell. In the non-standard setting referred to the parent phase ($\mathbf{a}, \mathbf{b}, \mathbf{c}$) the P_{a21} magnetic cell can be more simply described as $(2\mathbf{a}, \mathbf{b}, 2\mathbf{c})$. In the supplementary information we plot the refined magnetic structure with P_{a21} symmetry in these orthogonal axes (Fig. S3). The low resolution of D1B instrument prevents an accurate structural refinement of atomic positions so we fixed the fractional coordinates obtained from the refined data of x-ray patterns refining magnetic contribution using symmetry modes analysis. Within this formalism, the magnetic order is treated as distortions following the symmetry modes resulting from Irreducible representations of the undistorted parent crystal structure. The MSG P_{a21} has three available magnetic modes for each magnetic atom associated to the mA_1 irrep of the parent phase. Let us consider zig-zag chains of atoms running along a parallel to the ab plane as reference magnetic atoms (Pr-Pr-Pr-Pr or Fe-W-Fe-W, separately). The first mode (mA_1_1) corresponds to $\uparrow\uparrow\downarrow\downarrow$ Pr zig-zag chains ($\uparrow\cdot\downarrow\cdot$ for B-site cations) running along a of M_x magnetic moments. The configuration in the mode mA_1_3 is identical to the first but for M_z moments. Finally, the third magnetic mode (mA_1_2) shows the ‘up-down-down-up’ zig-zag chain along- a of M_y moments: $My(-My)(-My)My$ for Pr and $My(\cdot)(-My)(\cdot)$ for the B-site cations. The refinement of the magnetic modes clearly shows that the magnetic moments of Pr^{3+} and Fe^{2+} are collinearly oriented along the $[0, 1, 0]$ direction (see Fig. 7 and S3), i.e. parallel to the unique axis b ($=b_M$), as dictated by the magnetic mode mA_1_2 only.

The refined magnetic moments for Pr^{3+} and Fe^{2+} atoms at 5 K are $0.73(4) \mu_B$ and $1.90(2) \mu_B$, respectively showing a lack of full polarization of the magnetic moments. Regarding the interactions between different magnetic atoms, Fe atoms are at distances ranging between 3.37 and 3.58 Å from the four closest Pr^{3+} cations. The coupling is AFM with three of them and FM with the fourth (see Fig. S3). These data also unveil that magnetic ordering is collinear and differs from the non-collinear ordering reported earlier for $NaNdFeWO_6$ sample [18]. From our refinements we can discard a second magnetic component for the Fe arrangement in the Pr-based sample.

According to the magnetic point symmetry $2_11'$ of the low-temperature phase, the presence of a small net ferromagnetic component is forbidden by the P_{a21} symmetry. The FM component is at odd with the observed MSG or a pure AFM ordering. Its origin may be a magnetic impurity as indicated previously. This impurity is likely to be responsible for the ZFC-FC irreversibility in the Fig. 4(a). It worthwhile to note that the

occurrence of a rock-salt type cationic order at the B-site composed of magnetic Fe and non-magnetic W atoms causes the main magnetic interactions to be of Fe-O-O-Fe next-nearest-neighbor coupling [35, 36]. This is a weak magnetic interaction that can compete in magnitude with the direct Ln-Fe exchange coupling. These features are likely to be responsible for the low T_N and structural defects might account for the reduced magnetic moments. However, the relatively low ordered moment found concurs with the unusual behavior of the ZFC-FC susceptibility curves, signaling a possible complex and frustrated magnetic ground-state, only partially ordered in ZFC conditions.

3.4. Electrical properties.

The temperature dependence of the relative dielectric permittivity (ϵ_r') and dielectric loss ($\tan\delta$) for both samples at different frequencies (1kHz-1MHz) are shown in Fig. 8 between 10 and 310 K for the Pr-based sample while the same information for the Sm-based one can be found in the supplementary information (Fig. S4). A Debye-like relaxation with strong frequency dependence is observed in both samples. At low temperature, ϵ_r' tends to reach a similar value (around 17-18) for all frequencies in both samples. These values are of the same order of magnitude as those found in other ordered perovskites [37]. On warming, the dielectric constant is strongly enhanced at low frequencies while the increase is significantly smaller at high frequencies. No anomalies are observed suggesting a ferroelectric polarization or transition even at T_N . The P_{a21} MSG below T_N preserves the same point symmetry ($2_11'$) of the paramagnetic phase above T_N . Therefore, we do not expect qualitative changes in the evolution across T_N of the possible polarization P_y dictated by symmetry.

The dielectric loss also increases with the temperature and that increase is higher as the frequency decreases. However, a plateau is clearly observed in these curves. The plateau temperature increases with increasing frequency, suggesting that the dielectric relaxation is thermally activated. Similar features in other oxides are due to extrinsic effects such as Maxwell-Wagner type contributions of depletion layers at the interface between the sample and the electrodes or at grain boundaries [38-40]. The main difference between Pr- and Sm-based samples refers to the temperature of the step-like anomaly in the dielectric loss, which is higher for the latter compound. This might be related to the decrease of electrical conduction as the rare-earth size decreases, as suggested by the real part of the complex impedance (not shown here).

Ferroelectricity in doubly ordered perovskites, $AA'BB'O_6$, is a controversial subject. Combination of atomic orderings and cooperative tilts of BO_6 octahedra leads to the stabilization of an unit cell with $P2_1$ symmetry. This is a noncentrosymmetric space group which allows electric polarization along the unique axis. In this way, studies based on first principles and symmetry analysis [15] predicted a ferroelectric polarization of $\sim 16 \mu\text{C cm}^{-2}$ for NaLaMnWO_6 . However, experimental measurements performed on this sample [12] failed to find both second-harmonic generation (SHG) signal and spontaneous polarization using the PUND method, casting doubts about the actual symmetry of NaLaMnWO_6 . However, a clear SHG signal was obtained for NaLaFeWO_6 though no ferroelectric loop was found using the PUND method again [18]. Our structural refinements support the $P2_1$ symmetry for NaPrFeWO_6 and NaSmFeWO_6 and a predicted ferroelectric polarization $\sim 21\text{-}25 \mu\text{C cm}^{-2}$ (see section 3.1). With the aim of probing the ferroelectric properties of these compounds, electric-field-dependent polarization measurements, $P(E)$, were performed at different temperatures. At room temperature, the main contribution (not shown here) is purely resistive and the $P(E)$ loops have the characteristic circular shape. Moreover, both samples are not insulators and it is very hard to polarize them. On cooling, the samples become more insulating. Fig. 9 shows the loops obtained at 77 K for Pr-based sample (similar results were obtained for the Sm-based sample). The ellipsoidal shape is typical of a dielectric behavior with losses and shows the frequency dependence expected from the resistive contribution. This is a strong indication that electrical properties of these compounds are controlled by leakage currents [36] that could arise from oxygen vacancies. The results can be modeled using a parallel RC circuit as indicated in the supplementary information (see Fig. S5-S6). Our measurements showed that ferroelectricity is not observed for fields up to 8 kV cm^{-1} . Higher voltages were not possible due to the dielectric breakdown of the samples. The possible remanent polarization should be lower than $\sim 4 \text{ nC cm}^{-2}$ in our experimental conditions. This upper limit arises from the standard deviation found in the fit of our data to the parallel RC circuit. Therefore, there are no evidences of ferroelectric loop in these samples in agreement with previous results in related samples [12,18]. Bearing in mind the crystal structure of these compounds, there are several possibilities to explain this apparent contradiction. The first one is that these compounds are pyroelectric without switchable domains. Another possibility is a ferroelectric compound with coercive fields so high that are unreachable due to the leakage currents. In this way, the crystal structures refer

to ideal compounds and the actual compounds could exhibit different kinds of defects (vacancies, conductive grain boundaries, etc.) that could be detrimental for the stabilization of electric dipoles. Studies on single crystals (still non available) should be desirable to give a definitive response to this problem.

4. Conclusions.

We have synthesized two new members of the family of $AA'BB'O_6$ perovskites exhibiting an ordering of both A- and B-site cations. The structural characterization has determined that $NaPrFeWO_6$ and $NaSmFeWO_6$ adopt a noncentrosymmetric crystal structure with space group $P2_1$. Magnetic measurements show the occurrence of long range magnetic ordering of Ln^{3+} and Fe^{2+} magnetic moments at low temperatures and the presence of tiny magnetic impurities that dominate the magnetic response of both samples above T_N . Neutron diffraction measurements disclose a collinear antiferromagnetic structure following the propagation vector $\mathbf{k} = (\frac{1}{2}, 0, \frac{1}{2})$. The magnetic symmetry is P_a2_1 , and the Pr and Fe moments are all oriented along the $[0, 1, 0]$ direction following an ‘up-up-down-down’ sequence running along the $[1, 0, 0]$ direction. The magnetic order corresponds to the activation of the mA_{1_2} mode. The dielectric measurements indicate a dielectric response dominated by depletion layers at grain boundaries or electrodes without any evidence of ferroelectric ordering. The P(E) loops are characteristic of a dielectric material with losses coming most likely from leakage currents. This does not oppose the noncentrosymmetric nature of the crystal structure. The lack of ferroelectricity may be due to the fact that the material is composed by no switchable domains or the need for a perfect stoichiometry to avoid leakage currents. In this way, studies on single crystals would be desirable to ascertain the pyroelectric or ferroelectric nature of this system. Further synthetic and characterization efforts are also necessary to settle the evolution of the spin ordering in the $NaLnFeWO_6$ family of $AA'BB'O_6$ perovskites.

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Table 1. Atom fractional coordinates, occupancies and bond valence sums (BVS) for NaPrFeWO₆ at room temperature obtained from the Rietveld refinement (*) of the x-ray diffraction pattern. An average temperature factor was refined, $B_{av}=0.42(3) \text{ \AA}^{-2}$.

Atom	x	y	z	Occ.	BVS
Na/Pr	0.729(9)	-0.033(12)	0.49999(2)	0.97(1)/0.03(1)	0.94(8)
Pr/Na	0.75001(2)	-0.022(2)	-0.00001(4)	0.97(1)/0.03(1)	3.14(16)
Fe/W	0.742(4)	0.50001(2)	0.2553(7)	0.99(1)/0.01(1)	2.28(9)
W/Fe	0.7452(14)	0.49999(3)	0.7348(2)	0.99(1)/0.01(1)	5.96(23)
O1	-0.050(7)	0.221(7)	0.804(2)	1	-1.98(10)
O2	0.550(7)	0.779(7)	0.721(7)	1	-2.04(13)
O3	-0.019(7)	0.749(7)	0.804(2)	1	-2.01 (10)
O4	0.519(7)	0.251(7)	0.721(2)	1	-2.11(13)
O5	0.674(13)	0.559(13)	-0.009(3)	1	-2.02(16)
O6	0.798(13)	0.567(9)	0.516(3)	1	-2.16(13)

* All atoms are at the Wyckoff position $2a$. The refined lattice parameters are $a= 5.5294(5) \text{ \AA}$, $b= 5.5302(5) \text{ \AA}$, $c= 7.8950(2) \text{ \AA}$ and $\beta= 90.088(5)^\circ$. Na/Pr and Fe/W occupancies were refined with coupled parameters to yield the formal stoichiometry. Reliability factors are $R_p= 7.3\%$, $R_{wp}= 9.7\%$ and $R_{Bragg}= 3.7\%$.

Table 2. Atom fractional coordinates, occupancies and bond valence sums (BVS) for NaSmFeWO₆ at room temperature obtained from the Rietveld refinement (*) of the x-ray diffraction pattern. An average temperature factor was refined for all atoms, $B_{av}=0.32(7) \text{ \AA}^{-2}$.

Atom	x	y	z	Occ.	BVS
Na/Sm	0.680(5)	0.005(10)	0.4999(9)	0.96(1)/0.04(1)	1.13(7)
Sm	0.7500(10)	-0.021(2)	-0.0000(9)	0.96(1)/0.04(1)	3.15(10)
Fe	0.749(6)	0.5000(10)	0.2514(14)	0.99(1)/0.01(1)	2.45(10)
W	0.744(2)	0.4999(9)	0.7361(5)	0.99(1)/0.01(1)	5.81(21)
O1	-0.066(5)	0.205(5)	0.800(4)	1	-2.09(9)
O2	0.566(5)	0.795(5)	0.720(4)	1	-2.18(10)
O3	0.017(5)	0.712(5)	0.800(4)	1	-2.04(9)
O4	0.483(5)	0.288(5)	0.720(4)	1	-2.20(11)
O5	0.727(16)	0.55885	-0.004(5)	1	-2.09(10)
O6	0.779(15)	0.55318	0.506(5)	1	-1.93(14)

* All atoms are at the Wyckoff position $2a$. The refined lattice parameters are $a= 5.5346(3) \text{ \AA}$, $b=5.4608(3) \text{ \AA}$, $c=7.8769(4) \text{ \AA}$ and $\beta=90.120(7)^\circ$. Na/Sm and Fe/W occupancies were refined with coupled parameters to yield the formal stoichiometry. Reliability factors are $R_p= 9.6\%$, $R_{wp}=13.3\%$ and $R_{Bragg}= 5.1\%$.

Fig. 1. X-ray diffraction patterns for NaLaFeWO₆ (Ln=Pr, Sm, Eu, Gd and Tb) samples at room temperature with the indexation of the main diffraction peaks for a double perovskite. (*) and (#) mark the main peaks of Na₂WO₄ and NaLnWO₄, respectively.

Fig. 2. Observed (points), calculated (full line) and difference (bottom) x-ray diffraction profiles for (a) PrNaFeWO_6 and (b) SmNaFeWO_6 at room temperature. The bars denote the allowed reflections for the perovskite phase (top row) and the minor (<1%) impurity of NaLnWO_4 (bottom row).

Fig. 3. Projection on the ac plane of the P2₁ structure of NaPrFeWO₆ perovskites emphasizing the atom shifts (Fe and W) towards the Na plane. Broken line (crossing the octahedron centers) and arrows (shifts along c-direction) are guides for the eyes.

Fig. 4. (a) Temperature dependence of magnetization in ZFC (solid symbols) and FC condition (opens symbols) for NaPrFeWO₆ (blue on-line) and NaSmFeWO₆ (red on-line) at a field of 1 kOe. (b) ac magnetic susceptibility at three frequencies for NaSmFeWO₆ sample. Magnetic hysteresis loops at 5-300 K for (c) NaPrFeWO₆ and at 5-80 K for (d) NaSmFeWO₆ samples. The lines correspond to the fits to the formula (1) as indicated in the text.

Fig. 5. Inverse of the ac magnetic susceptibility vs. temperature for (top) NaPrFeWO₆ and (bottom) NaSmFeWO₆. The data were collected using a dc field of 20 kOe and ac field of 4 Oe with a frequency of 11 Hz. The straight line shows the fit to the Curie-Weiss law, $\chi' = C/(T - \theta)$, in the 100-300 K temperature range. The fitted parameters are also shown in the plot.

Fig. 6. (a) Neutron thermodiffractograms of NaPrFeWO₆ with the indexation of the new magnetic peaks at low temperature. (b) Pattern obtained by the difference between the neutron patterns collected at 50 and 2 K for NaSmFeWO₆. Weak magnetic peaks are noticeable and indexed to facilitate the comparison with the top panel.

Fig. 7. a) Rietveld analysis of the neutron diffraction pattern for NaPrFeWO_6 at 5 K. Bars stand for allowed reflections of the analyzed phases. First row correspond to the main NaPrFeWO_6 phase while 2nd and 3rd rows correspond to NaPrWO_4 and $\text{Na}_2\text{WO}_4 \cdot 2(\text{H}_2\text{O})$ impurities, respectively. (b) Crystal and magnetic structure of NaPrFeWO_6 at 5 K.

Fig. 8. (a) Temperature dependence of the dielectric constant (ϵ') and (b) the dielectric loss ($\tan \delta$) for NaPrFeWO₆ at five selected frequencies. Insets: Details of the measurements at low temperature.

Fig. 9. Top: $P(E)$ loops for NaPrWFeWO_6 sample collected at 77 K and at different amplitudes of the electric field. Bottom: $P(E)$ loops for NaPrWFeWO_6 sample collected at 77 K and at two different frequencies of the sinusoidal excitation voltage of 800 V .