A new type of antiferrodistortive structure in a double perovskite with Pb

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ABSTRACT

We find a new structural transition in $\text{Pb}_2\text{MnReO}_6$ at 410 K. Above this temperature, $\text{Pb}_2\text{MnReO}_6$ is cubic with disordered and dynamic atomic displacements manifested in the large thermal parameters of Pb and O atoms. Below 410 K, the antiferrodistortive shift of 2/3 of Pb^{2+} cations away from the high-symmetry cubic site produces a new type of monoclinic cell. The unit cell expands at the transition and the heat capacity shows a peak with thermal hysteresis. These features agree with a first order transition. The entropy content of the transition is quite low indicating that the structural disorder has not been completely removed in the low temperature phase.

The monoclinic phase of $\text{Pb}_2\text{MnReO}_6$ shows thermally activated conductivity which does not vary when an external magnetic field is applied. A change in the slope of the resistivity curve, observed at the structural phase transition temperature, is related to a slight difference in the activation energy between both phases. It suggests that the condensation of the distortions likely affects the conduction mechanism. The isothermal magnetization measurements reveal the presence of ferromagnetic contributions below 85 K. The ac magnetic susceptibility shows a dynamic peak at 50 K and, in addition, zero-field-cooled and field-cooled magnetization curves diverge strongly below 80 K. These features might be signature of magnetic inhomogeneity. Magnetic loops, obtained at 5 K, do not show saturation in fields up to 9 T. Furthermore, the measured coercivity increases sharply at low temperature indicating an abrupt change in the magnetic anisotropy. We show that all these magnetic properties point out to a ferrimagnetic ordering of Mn and Re atoms in an intermediate valence state.

1. Introduction.

Materials which integrate magnetic and electric orderings are of great interest since they show not only intriguing physical properties¹ but they are also attractive for technological applications.²⁻³ The most useful attribute is the coupling between electric and magnetic properties which gives rise to the magnetoelectric effect. This effect has been found recently in several oxides with perovskite-like structures.¹⁻⁶ The perovskite oxide, ABO_3 , has space group $Pm\bar{3}m$ with a 12-fold coordinated large cation (A) and an octahedrally coordinated smaller cation (B). The solid solution of type $AB_{1-x}B'_xO_3$ is commonly found for these compounds. However, if the B and B' cations differ in oxidation state or in size or in both, then the B-site cations are very likely to order in a rock-salt pattern. Consequently, the new phase is described by the formula $A_2BB'O_6$ for $x=0.5$ and is denoted as double perovskite (also elpasolite).⁷⁻⁹ Ferro- and antiferromagnetic B-B' couplings are usually observed in these compounds and in some cases, even with a non-magnetic B element.¹⁰

A current research activity in the field of double perovskites is motivated by the finding that the stereochemical activity of the $6s^2$ lone pair could favour the coupling between ferroelectricity and magnetism. Such mechanism might take place in Bi^{3+} and Pb^{2+} double perovskites with magnetic interactions between B and B' cations. The above strategy has mainly been used for Bi-based compounds.^{6,11} However, $Pb_2BB'O_6$ compounds have been known for a long time.¹²⁻¹⁴ In these compounds, the Pb usually adopts distorted environments which arises from displacements of Pb ions out from the centre of the oxygen coordination polyhedra. The displacements may occur along either the [100] cubic direction as reported for Pb_2CoWO_6 and Pb_2MnWO_6 double perovskites^{15,16} or the [111] cubic direction as in the Pb_2ScSbO_6 compound.¹⁷ In most cases, reported studies focused on electrical properties of samples with non-magnetic B-cations. Here, we report results of a study on Pb_2MnReO_6 , where both Mn and Re have unpaired d electrons and the superexchange rules predict a ferrimagnetic ground state. Indeed, a magnetic transition was found below 100 K but, surprisingly, no distortive displacements of the Pb-cation have been reported in an earlier work.¹⁸ The crystal structure at room temperature has been refined as a monoclinic double perovskite (space group $P2_1/n$) arising from

cooperative tilts of the BO_6 octahedra. Apparently, the stereochemical activity of the $6s^2$ lone pair in Pb^{2+} has been quenched for this compound.

In the course of our search for double-perovskites with enhanced multiferroic properties, we have depicted the para-antiferroelectric phase transition in Pb_2MnWO_6 which occurs at 423 K.^{16,19} This compound also undergoes a structural phase transition at the same temperature.¹⁶ The high temperature phase is cubic and transforms into an orthorhombic structure with collinear antiferroelectric displacements of Pb^{2+} cations. These atoms have a distorted first coordination shell. EXAFS spectroscopy reveals a similar local disorder around Pb atoms for both cubic and orthorhombic phases.¹⁹ Hence, dynamic disordered distortions exist in the cubic phase, which freeze in an ordered pattern below 423 K, and the transition can be classified as an order-disorder type. We expected that the replacement of W by Re would affect the magnetic properties of the system but we did not suspect that this substitution will deeply modify the local structure for Pb^{2+} .

A likely coupling between magnetism and crystal structure motivated us to carry out a careful characterization of the crystallographic, electrical and magnetic properties of $\text{Pb}_2\text{MnReO}_6$. It is noteworthy that the stoichiometry of this compound is highly dependent on the synthetic conditions. The perovskite structure can only be obtained at relatively low temperature. At higher temperatures, a competitive pyrochlore phase is formed.¹⁸ We successfully synthesized the perovskite phase with a full Mn-Re ordering at the octahedral sites for the first time. We found that this system undergoes a structural phase transition above room temperature, similarly to Pb_2MnWO_6 . Our results show a new type of monoclinic cell at room temperature. This monoclinic structure actually shows antiferroelectric movements of some Pb atoms in a way not previously observed in any other double perovskite. Electrical and magnetic properties reasonably agree with the ones previously reported.¹⁸ Slight differences might be ascribed to the different synthetic route used in the present work that allowed us to prepare a sample free of antisite defects. The reported structural phase transition is accompanied by an anomaly in the resistivity curve. A ferrimagnetic ordering of Mn and Re atoms in a mixed valence state is also observed below 85 K.

2. Experimental Section.

$\text{Pb}_2\text{MnReO}_6$ was prepared by solid state chemistry reaction. Stoichiometric amounts of PbO , MnCO_3 and ReO_3 were mixed, ground, pressed into pellets and heated in an Ar stream at 710°C for 2 h twice with an intermediate ground. Previous synthesis was carried out at 550°C for 12 h and the starting precursors were Re_2O_7 , Mn_2O_3 and PbO .¹⁸ We have observed that the perovskite phase is formed faster (kinetically controlled product) than the pyrochlore phase (thermodynamically controlled product) and the direct synthesis at higher temperature with shorter reaction times also yields a pure perovskite phase. The temperature limit is around 725°C . Above this limit, significant amount of pyrochlore phase is formed while below this temperature the reaction time is also important because long reaction times favour the appearing and growing of the pyrochlore phase. The use of ReO_6 and MnCO_3 precursors, with the appropriate cationic valences, also seems to favour the kinetic control of the chemical reaction. The increase in the temperature reaction improves the Re-Mn ordering as occurs in related double perovskites.²⁰

The resulting pellet was black with a high electrical resistivity. The sample was characterized by x-ray powder diffraction using a Rigaku D-Max system. Step-scanned patterns were measured between 10° and 130° (in steps of 0.03°) at room temperature. The x-ray system was working at 40 kV and 100 mA with a counting rate of 4 sec.step⁻¹. We used a graphite monochromator to select the Cu K_α radiation. The medium and low temperature chamber manufactured by Rigaku was coupled to the goniometer to measure patterns between 123 and 523 K. In this case, the angle range was between 10° and 120° with the same step. The crystal structures were refined by the Rietveld method using the Fullprof package program.²¹

Differential scanning calorimetry (DSC) was measured using a DSC Q-20 from TA-Instruments with samples sealed in aluminium pans under a nitrogen atmosphere. The scanning rate was 10 Kmin^{-1} . Magnetic measurements were performed between 5 and 300 K in a commercial Quantum Design superconducting quantum interference device (SQUID) magnetometer. Resistivity measurements were carried out using the standard six-probe AC method in the temperature range between 80 and 500 K. An

electromagnet, which provides magnetic fields up to 1 T, was used to test the magnetoresistance properties.

3. Results and discussion

3.1. Structure. Our crystallographic study reveals that $\text{Pb}_2\text{MnReO}_6$ undergoes a structural phase transition upon heating above room temperature, which resembles the one observed in the Pb_2MnWO_6 system.¹⁶ Figure 1 shows the x-ray diffraction pattern collected at 523 K. This measurement confirmed that our sample was almost single phase with only a tiny impurity (0.9% in weight) identified as a pyrochlore phase with a similar chemical composition. The secondary phase was included in the refinement using the structural data reported previously.¹⁸ At 523 K, $\text{Pb}_2\text{MnReO}_6$ adopts the ordered cubic perovskite structure with the space group $Fm\bar{3}m$. The Rietveld refinement confirms a full Mn-Re ordering without significant presence of antisite defects (i.e. Mn-Re substitution disorder). This is an important difference with the previous study on $\text{Pb}_2\text{MnReO}_6$ where 15% of antisite disorder was found.¹⁸ The difference might come from the higher synthesis temperature used in the present study as it is indicated in the experimental section. The structural parameters derived from the refinement of this pattern are summarized in tables 1 and 2. Unusual large temperature factors associated with the Pb and O sites indicate the presence of disordered atomic displacements in the cubic phase. Similar results have been reported in the cubic phases of other Pb-based double perovskites and they have been ascribed to the dynamic distortions induced by the stereoactive electron lone-pair of Pb^{2+} .¹⁴⁻¹⁷

Table 3 reports selected interatomic distances obtained from the structural refinement. Regarding the Pb-O polyhedron, the experimental value reported in table 3 agrees with the theoretical estimation of 2.87 Å for Pb^{2+} -O distance. The distances obtained for the cubic phase reveal the presence of regular MnO_6 and ReO_6 octahedra. Assuming the tabulated ionic radii,²² the calculated values for Mn^{2+} -O, Mn^{3+} -O, Re^{5+} -O and Re^{6+} -O bond lengths should be 2.23, 2.085, 1.98 and 1.95 Å, respectively. The comparison to the experimental values of table 3 suggests an intermediate valence for Re and a valence close to +3 for Mn ion. However, experimental Mn^{2+} -O distances found in Mn-based double perovskites^{16,23} range between 2.12 and 2.14 Å. Therefore, we can assume an intermediate valence for

Mn in the $\text{Pb}_2\text{MnReO}_6$ as well. In this way, $\text{Mn}^{2.5+}$ and $\text{Re}^{5.5+}$ seem to be the most plausible intermediate valence states for the $\text{Pb}_2\text{MnReO}_6$ double-perovskite.

Upon decreasing the temperature, two changes occur in the x-ray diffraction patterns below 390 K, as can be observed in Fig. 2. One is the peak splitting that develops in many of the strong diffraction lines. The second change is the appearing of a number of new superstructure peaks as is shown in the inset of Fig. 2. The splitting of the peaks can be accounted for by the monoclinic cell reported in Ref. 18 (space group $P2_1/n$). This cell forms from the cooperative tilts of MnO_6 and ReO_6 octahedra, following the system tilt denoted as $a^-a^-c^+$ in the Glazer's terminology.²⁴ However, an exhaustive inspection of the x-ray patterns casts doubts on such interpretation. In addition, a monoclinic cell with space group $I2/m$ also fits the main peaks of the pattern. The latter monoclinic cell corresponds to the $a^0b^-b^-$ tilt system.²⁴ In any case, both these models fail to reproduce the intensity of the most important new superstructure peaks indicating that not only cooperative octahedra tilts but also atomic shifts are responsible for their presence. Details of the refinements using $I2/m$ and $P2_1/n$ space groups are available in the additional supporting information accompanying this article. The indexation of the main superstructure peaks using the high temperature structure (inset of Fig. 2) suggests the need to treble a monoclinic axis (a face diagonal of the high temperature phase). In order to test it, we have verified by means of a Le Bail refinement²⁵ that these new lines can be indexed after trebling the b-axis, i.e. within a monoclinic cell with lattice vectors $(\frac{1}{2}, \frac{1}{2}, 0)$, $(-\frac{3}{2}, \frac{3}{2}, 0)$ and $(0, 0, 1)$ with respect to the parent structure. Only four very weak reflections that we will discuss later on were not indexed (two of them are underlined in the inset of Fig. 2).

In order to explore the possible atomic displacements able to give the mentioned triple monoclinic cell, we have used the ISODISPLACE tool.²⁶ This software allows us to explore structural phase transitions by generating atomic displacement patterns corresponding to irreducible representations of the parent space-group symmetry. Accordingly, we have used the cubic double perovskite structure (high temperature phase) as the parent compound and we have searched over arbitrary k-points of the first Brillouin zone in order to obtain the mentioned 'triple' monoclinic cell or related ones. A detailed

inspection of the active modes for the different solutions revealed that the main superstructure peaks arise from the condensation of a Σ_2 mode at the $(2/3, 2/3, 0)$ k-point. Three solutions were retained as the most plausible candidates and they are summarized in table 4. Among these solutions, the C-centred lattice implies the least amount of active modes and, therefore, fewer parameters to be refined. In order to test it, we have used the AMPLIMODES program²⁷ from the Bilbao Crystallographic Server to obtain an input file for Fullprof. The structural analysis consists of decomposing the symmetry-breaking distortion, present in the transition from $Fm\bar{3}m$ to $C2/m$, into contributions from various symmetry-adapted modes. The amplitude refinement of the basis modes reaches convergence easily and gives rise to an accurate fit as the one shown in the Fig. 2. Details of the model and the final atom positions are summarized in tables 1 and 2, respectively. The refined global amplitudes are indicated in table 4. We have performed similar refinements using the other two solutions of table 4 and we obtained similar good fits if only the same modes present in the $C2/m$ cell were used. Additional modes, specific to $P2_1/c$ or $P2/c$ cells, have negligible contribution in the refinement process. It strongly suggests that the $C2/m$ solution is the simplest model accounting for the x-ray pattern. The only exception are four very weak peaks indexed in the frame of the parent compound as $(4/3, 4/3, 5/2)$, $(2/3, 2/3, 7/2)$, $(2/3, 2/3, 9/2)$ and $(14/3, 14/3, 3/2)$. Two of them are marked in the inset of fig. 2 for the sake of comparison. These lines point to the doubling of another axis. The symmetry analysis yields as a possible solution a primitive monoclinic cell whose lattice vectors respect to the parent compound are $(-1/2, -1/2, 0)$, $(0, 0, 2)$ and $(-1, 2, 0)$. We have checked that a Le Bail refinement using the highest possible symmetry ($P2_1/c$ space group) can account for all diffraction peaks. However, it contains 90 amplitudes of basis modes whose refinement is out of the accuracy of our conventional x-ray powder diffraction patterns. Therefore, we have retained the $C2/m$ solution as the best structural approximation for $\text{Pb}_2\text{MnReO}_6$.

The crystal structure of $\text{Pb}_2\text{MnReO}_6$ at room temperature is a new type of monoclinic structure that has not been reported, up to the best of our knowledge, in the field of double perovskites. In this structure, the crystallographic site of Pb, Mn, and Re atoms is split into two non-equivalent sites with a ratio of 2 to 1. The oxygen has 8 non-equivalent sites in the $C2/m$ cell. Such crystal structure can be

understood as arising from the conventional cubic structure of a double perovskite by the combined condensation of two modes of atomic displacement, Γ_4^+ and Σ_2 . The first one is associated to the anti-phase tilts of BO_6 octahedra about the y -direction in the monoclinic cell (or about the unique axis). Figure 3 shows a projection of the crystal structure onto the ac -plane emphasizing these tilts. The mode Σ_2 is associated to atomic shifts of the atoms located at some specific Wyckoff positions. The main shift corresponds to the Pb atoms placed at the $8j$ positions (denoted as Pb2 in the table 2). This mode does not affect the Pb situated at the $4h$ site (Pb1). The Pb2 atoms are shifted by $\sim 0.177 \text{ \AA}$ away from the ideal cubic position along the monoclinic z -direction which correspond to the $[1\ 1\ 0]$ direction in the high temperature phase. The shift is in the opposite directions ($+z$ and $-z$) for successive rows of Pb2 atoms giving rise to the antiferroelectric configuration indicated by arrows in Fig. 3. Only two thirds of the Pb atoms are shifted in opposite directions whereas the other third (Pb1) remains fixed at $z=1/2$.

The Σ_2 mode also affects Mn atoms at one of the Mn sites although in lower proportion. Its contribution to the Re atoms is negligible. The remaining modes can be considered as secondary but they also play a role. For instance, the Σ_1 mode is associated with an antiphase displacement between Pb1 and Pb2 atoms along the y -direction. Γ_5^+ , in addition to Σ_2 , leads to oxygen displacements which distort the octahedral environment around Mn and Re atoms (see Fig. 3).

Regarding the atom bonds, there are significant differences between both crystallographic phases. Pb has a 12-fold coordination in the high temperature phase. Similar coordination with almost the same average Pb-O distance remains for the Pb1 in the monoclinic phase (see table 3) although the local environment is more distorted. However, the atomic displacement of Pb2 atoms reduces their effective coordination to 9 and shortens the average Pb2-O bond length. In the case of Mn atoms, a distortion in the octahedral coordination is observed in the monoclinic phase with a slight difference in the size of MnO_6 octahedra. Similar features are observed for the ReO_6 octahedra but, in this case, the distortion is larger and both ReO_6 octahedral expand through the transition to the monoclinic phase. Accordingly, the Re-O bond length increases towards the expected values for $\text{Re}^{5+}\text{-O}$.

The temperature dependence of the lattice parameters upon decreasing the temperature from 523 K down to 123 K is displayed in Fig. 4. The structural transition is observed at 410 K. Above this temperature, the cubic lattice parameter follows the typical thermal expansion on warming. Below 410 K, only the monoclinic *c*-axis contracts monotonically on cooling. The other two monoclinic axes show anomalous behaviour: the *b*-axis abruptly shrinks for and the *a*-axis expands strongly. These changes produce an abrupt increase of 0.23 Å³ in the unit cell volume per formula unit at the transition on cooling. Similar results were found for the structural transition of Pb₂MnWO₆.¹⁶ Away from the transition region, the thermal expansion is positive in the whole temperature range studied although with different slopes for each phase. The volume expansion coefficient is 1.56×10⁻³ Å³×K⁻¹ for the monoclinic phase (between 123 and 373 K) but it reaches a value of 5.44×10⁻³ Å³×K⁻¹ in the cubic phase between 423 and 523 K. The evolution of the volume per unit formula versus temperature is included in the additional supporting information.

3.2. Heat capacity. The phase transition was also characterized by DSC measurements whose results are displayed in Fig. 4. Heat capacity shows a rounded peak at approximately 413 K, in agreement with the change observed in the crystal structure. We have measured heating and cooling scans at the speed of 10 K min⁻¹. A clear shift of 6 K is observed which agrees with a first order transition. The phase-transition enthalpy, $\Delta H = \int \Delta C_p(T) dT$, is 768 ± 58 J mol⁻¹. The total change in the entropy is $\Delta S = 1.86 \pm 0.15$ Jmol⁻¹ K⁻¹. This value is approximately equal to 0.22*R*, *R* being the gas constant. The obtained value of entropy is smaller than the ones found for other double perovskites, which are usually close²⁸ to *R* ln 4. In addition, it is only one third of the corresponding value for the transition in Pb₂MnWO₆.¹⁶ However, it is quite close to the entropy change observed in the structural transition of Pb₂MgTeO₆ (~0.3*R*) which was ascribed to the presence of structural disorder in the low temperature phase.²⁹ In our case, large temperature factor has been refined for Pb1 at room temperature (see table 3) suggesting that dynamic disorder is still present for this crystallographic site.

3.3. Electrical properties. The electrical resistivity was measured from 500 down to 80 K. Below this temperature, the resistivity was too high to be measured reliably. The Pb₂MnReO₆ system is

semiconducting in the temperature range studied (Fig. 5). It shows an anomaly in the curve slope at the structural transition temperature which is clearly seen in the plot of $\ln\rho$ vs. $1/T$ exhibited in the inset of Fig. 5. Above and below the phase transition temperature, the Arrhenius law is obeyed. The change in the slope is then ascribed to an increase of the activation energy at the transition which can be related to the enlargement of the energy gap in the low temperature phase. Above the transition, the linear fit gives the activation energy of 0.135 eV whereas below the transition, the linear fit works down to 150 K (see additional information) and the activation energy is 0.19 eV. Overall, the later value agrees with the ones reported in Ref. 18; the slight difference may be ascribed to the different degree of antisite disorder. We have repeated the electrical measurement under an external field of 1 T. No differences have been found between both curves indicating a negligible magnetoresistance in these conditions.

Attempts of characterizing the dielectric permittivity at the structural transition were unsuccessful due to the high electronic conductivity of the sample. The electrical resistivity measured at 300 and 400 K was ~ 2 and $\sim 0.27 \text{ } \Omega\cdot\text{cm}$, respectively. Therefore, possible anomalies in the dielectric constant were masked by the high conductivity of the material. Consequently, an ordering of electric dipoles at the transition cannot be excluded.

3.4. Magnetic properties. The temperature dependence of the dc magnetization was measured using zero-field-cooling (ZFC) and field-cooling (FC) conditions at two applied magnetic fields as can be seen in the Fig. 6. At 500 Oe, the ZFC curve shows a peak at 40 K and a divergence between FC and ZFC curves begins at 77 K. These features strongly depend on the magnetic field strength. At 5 kOe, the maximum in the ZFC curve is observed at 20 K and the magnetic irreversibility starts at 47 K. In both cases, the FC curves behave as expected for a ferri- or ferromagnetic transition.

The ac magnetic susceptibility (χ_{ac}) shows a broad maximum at 51 K whose intensity depends on the frequency of the alternating field (see inset of Fig. 6). There is no significant shift of the magnetic peak in the frequency range studied (17-999 Hz). Both properties, magnetic irreversibility in dc magnetization and dynamical ac susceptibility, are usually ascribed to the formation of magnetic clusters with no long range magnetic ordering. However, double perovskites showing long-range order

exhibit similar properties that were explained as arising from vibrations of domain-wall within a pinning potential produced by local anisotropy.³⁰ Neutron diffraction is therefore needed to elucidate this point. χ_{ac} clearly does not obey a Curie law below 100 K but the χ_{ac}^{-1} vs T plot (Fig. 7) was fitted to the Curie-Weiss law in the range 150-360 K yielding a Weiss temperature of $\theta \sim -32$ K and an effective paramagnetic moment of $\rho_{eff} = 5.66 \mu_B$ per formula unit. The negative θ indicates predominant antiferromagnetic exchange interactions and its value is close to the temperature at which the peak in the ZFC curve of dc magnetization measurements is observed. ρ_{eff} is smaller than the spin-only value for a high spin Mn^{2+} ion ($5.90 \mu_B$) but it nicely agrees with the expected contribution for non-interacting Mn^{3+} - Re^{5+} paramagnetic array ($5.65 \mu_B$ for spin-only contributions). However, an intermediate $Mn^{2.5+}$ - $Re^{5.5+}$ valence state was deduced from the refined bond lengths summarized in table 3. Assuming that the paramagnetic state could be modelled by an array of x (Mn^{2+} - Re^{6+}) and (1-x) of (Mn^{3+} - Re^{5+}) ionic couples, the effective paramagnetic moment would be $(\rho_{eff})^2 = x \cdot [(\rho_{Mn}^{2+})^2 + (\rho_{Re}^{6+})^2] + (1-x) \cdot [(\rho_{Mn}^{3+})^2 + (\rho_{Re}^{5+})^2]$. If we consider spin-only values for the Mn cations and the total angular momentum J for the Re cations, the experimental effective paramagnetic moment yields a value of x=0.51, which supports the description in terms of intermediate valence states. The use of J values for Re atoms is justified by the fact that circular dichroism measurements have found orbital moments of $0.3 \mu_B$ per Re atom in related double perovskites.³¹ Therefore, significant spin-orbit coupling is found in Re ions and the angular moment is not quenched for this 5d-ion in the system studied.

Fig. 8 shows magnetic loops at selected temperatures. Ferromagnetic contribution is observed at 85 K whereas the sample behaves as a conventional paramagnet at 95 K. Upon cooling, both the spontaneous magnetization and the coercive field increase. The hysteresis cycle at 5 K does not reach magnetic saturation at 5 T. In order to check it, magnetic loops were measured at 5 K in a Quantum Design ppms system using magnetic fields up to 9 T but the saturation is not achieved even at this field as can be seen in the additional information. Absence of magnetic saturation, under an applied field as high as 30 T, was found for several Re-based double perovskites.³²⁻³³ This property was ascribed to the existence of

large disorder at the grain boundary regions which are magnetically harder than the grain core. The obtained magnetic moment is $2.22 \mu_B/\text{f.u.}$ at 9 T. This value is significantly smaller than the expected one for a ferrimagnetic ordering of $\text{Mn}^{2+}/\text{Re}^{6+}$. However it is larger than the expected value for $\text{Mn}^{3+}/\text{Re}^{5+}$ order, in agreement with the conclusions of intermediate valences for both Mn and Re atoms.

The hysteresis loops provides more interesting information. The initial magnetization curves are in agreement with a pinning-type magnet³⁴ which may be related to the irreversibility effects observed in the Fig. 6. This is not surprising because this is a ceramic material with grain boundaries and, furthermore, defects such as vacancies or dislocations are likely to occur. The loop at 5 K exhibits a remanence of $0.79 \mu_B/\text{f.u.}$ This remanence decreases with the temperature. The temperature dependence is not linear but it follows a sigmoid-like function (inset A of Fig. 8). The most striking point is the anomalous temperature dependence for the coercive field $H_C(T)$. The temperature coefficient is negative in the whole temperature range but a strong increase of the coercive field is observed below 25 K (inset B of Fig. 8). The presence of defects could explain the large coercive fields but it is very unlikely that a sudden change in the pinning forces would occur with decreasing the temperature. Therefore, this anomaly can be attributed to an abrupt increase of the magnetocrystalline anisotropy.

4. Conclusions

$\text{Pb}_2\text{MnReO}_6$ can be prepared by conventional ceramic procedures. It belongs to the family of double perovskites with an ordered arrangement of Mn and Re atoms in the B-sublattice. The reported sintering at 710°C clearly favours a full Mn-Re ordering. We have shown that this compound undergoes a structural phase transition at 410 K from a cubic ($Fm\bar{3}m$) to a monoclinic ($C2/m$) cell on cooling. This transition is driven by the condensation of two primary modes: Γ_4^+ associated to the anti-phase tilting of BO_6 octahedra about the unique b-axis and Σ_2 associated to the collinear movement in opposite directions of some atoms, in particular of 2/3 of the Pb^{2+} cations. To the best of our knowledge, this type of antiferrodistortive structure has not been reported in the field of double perovskites.

The structural transition is associated with an anomaly in the thermal expansion of the unit cell due to a significant difference between the volumes of the high and low temperature phases. The variation of lattice constants is anisotropic because on warming, the monoclinic *a*-axis shrinks at the transition temperature whereas the *b*-axis expands. The entropy content for the transition is smaller than the one expected for an order-disorder transition indicating the presence of significant disorder in the low temperature phase. The phase transition is also accompanied by anomalies in the electrical resistivity related to an increase of the activation energy upon cooling the sample.

The magnetic measurements reveal the presence of ferrimagnetic interactions at low temperatures. However, the observed irreversibility in the magnetization curves and dynamic behaviour of the ac susceptibility could be as well due to magnetic inhomogeneities with the presence of either spin-glass region or a reentrant transition. Domain wall pinning effects in long range ferrimagnetic systems could also account for these properties. Neutron diffraction experiments are therefore desirable to clarify this subject.

A sharp increase of the coercive field in the hysteresis loops reveals an abrupt change in the magnetocrystalline anisotropy whose origin might be associated to structural changes in the ferrimagnetic phase. The sample does not achieve magnetic saturation at 9 T and at 5 K but the paramagnetic region follows a Curie-Weiss law. Both the effective paramagnetic moments and the magnetization at 9 T do not fit to Mn^{2+} and Re^{6+} valences for the B-sublattice. Our result point out to a mixed valence character ($\text{Mn}^{2+\delta}$ and $\text{Re}^{6-\delta}$; $\delta \sim 0.5$), also supported by the refined bond lengths obtained in the structural study.

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Supporting Information Available: Details of the refinements using $P2_1/n$ and $I2/m$ models. Plots of the volume thermal expansion range, of the activated conductivity and of the isothermal magnetization at 5 K and up to 9 T.

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FIGURE CAPTIONS

Figure 1. Rietveld refinement of x-ray powder diffraction pattern of $\text{Pb}_2\text{MnReO}_6$ at 523 K. Observed (points), calculated (line) and the difference below the pattern. The vertical bars correspond to the calculated peak positions for the perovskite (1st row) and pyrochlore (2nd row) phases. Arrow marks the main peak of the secondary phase. Inset: Picture of the cubic structure for $\text{Pb}_2\text{MnReO}_6$. Balls denote Pb atoms while dark (red online) and light (yellow online) octahedra stand for MnO_6 and ReO_6 , respectively.

Figure 2. Rietveld refinement of x-ray powder diffraction pattern of $\text{Pb}_2\text{MnReO}_6$ at 300 K. Symbols corresponds to the ones of Fig. 1. Inset: Detail of the refinement emphasizing some of the superstructure peaks. The underlined indexes show two very weak peaks not accounted for by the model $C2/m$. Asterisk marks the main pyrochlore peak.

Figure 3. Crystal structure of $\text{Pb}_2\text{MnReO}_6$ projected along the ac -plane at room temperature. Balls stand for Pb atoms while dark (red online) and light (yellow online) octahedra stand for MnO_6 and ReO_6 , respectively. Arrows indicate the direction for Pb displacements. The unit cell vectors are also indicated.

Figure 4. Temperature evolution of the lattice parameters for $\text{Pb}_2\text{MnReO}_6$. The monoclinic a and c axes has been multiplied by the shown factors for the sake of comparison. DSC scans on cooling and heating at 10 K min^{-1} .

Figure 5. Electrical resistivity vs. temperature for $\text{Pb}_2\text{MnReO}_6$. The line and points indicate the measurements under 0 and 1 T, respectively. Inset: $\ln\rho$ vs. $1/T$ between 300 and 500 K. The lines show the fits to the Arrhenius law above (500-420 K) and below (405-300 K) the structural phase transition temperature ($\sim 410 \text{ K}$). The calculated activation energies are also indicated in the figure.

Figure 6. Dc magnetization vs temperature for $\text{Pb}_2\text{MnReO}_6$. Circles and squares correspond to the measurements under fields of 500 and 5000 Oe. Solid symbols refers to ZFC conditions while open symbols stand for FC conditions. Inset: Ac magnetic susceptibility at frequencies of the alternating field of (from top to bottom) 17, 99 and 999 Hz.

Figure 7. Inverse of the ac magnetic susceptibility vs. temperature for $\text{Pb}_2\text{MnReO}_6$. The line represents the Curie–Weiss fit obtained between 150 and 360 K. The fit parameters and the effective paramagnetic moment are also shown.

Figure 8. Isothermal magnetization of $\text{Pb}_2\text{MnReO}_6$ at the temperatures indicated in the plot. The data at 15 and 25 K have been omitted for the sake of clarity. The insets show the temperature dependence for the remnant magnetization (inset A) and coercivity (inset B) of the hysteresis loops.

	523 K	300 K
Space group	$Fm\bar{3}m$	$C2/m$
a (Å)	8.1098(2)	18.2309(9)
b (Å)	-	8.0359(2)
c (Å)	-	5.7072(2)
β (deg)	-	108.288(2)
Vol. (Å³)	533.38(2)	793.88(5)
Z	4	6
No. reflections	97	858
Refined parameters	15	32
R_p (%)	5.9	4.6
R_{wp} (%)	8.0	6.4
R_{Bragg} (%)	2.1	3.7

Table 1. Refined lattice parameters, unit cell volume and refinement data for Pb₂MnReO₆. The number of reflections and refined parameters only concerns to the main perovskite phase. The reliability factors are defined in ref. 21.

atom	site	x/a	y/b	z/c	B ($\text{\AA}^2$)
<i>Cubic cell at 523 K</i>					
Pb	8c	1/4	1/4	1/4	2.65(3)
Mn	4b	1/2	1/2	1/2	0.34(2)
Re	4a	0	0	0	0.18(2)
O	24e	0.2419(6)	0	0	2.62(15)
<i>Monoclinic cell at 300 K</i>					
Pb1	4h	0	0.7388(4)	1/2	1.62(14)
Pb2	8j	0.8333	0.2502(3)	0.8022(2)	0.76(5)
Mn1	2a	0	0	0	0.21(7)
Mn2	4i	0.8333	1/2	0.3131(11)	0.21(7)
Re1	2b	0	1/2	0	0.09(2)
Re2	4i	0.8333	0	0.3333	0.09(2)
O1	4g	0	0.7417(5)	0	0.79(16)
O2	4i	0.7421(9)	1/4	0.0324(18)	0.79(16)
O3	4i	0.2265(9)	1/4	0.422(3)	0.79(16)
O4	8j	0.8333	0.2417(5)	0.345(2)	0.79(16)
O5	4i	0.5890(10)	1/2	0.339(2)	0.79(16)
O6	4i	0.0912(9)	1/2	0.3010(18)	0.79(16)
O7	4i	0.0598(9)	1/2	0.756(3)	0.79(16)
O8	4i	0.5933(10)	1/2	0.857(4)	0.79(16)

Table 2. Wyckoff positions, refined fractional atomic coordinates and isotropic temperature factors for $\text{Pb}_2\text{MnReO}_6$. An only temperature factor was refined for all oxygen atoms in the monoclinic cell.

Cubic at 523 K		Monoclinic at 300 K			
Pb-O ($\times 12$)	2.868 (4)	Pb1-O1 ($\times 2$)	2.8537	Pb2-O1	2.8911(1)
		Pb1-O4 ($\times 2$)	2.890(4)	Pb2-O2	2.762(11)
		Pb1-O5 ($\times 2$)	2.970(13)	Pb2-O3	2.448(8)
		Pb1-O6 ($\times 2$)	2.987(13)	Pb2-O3	2.610(11)
		Pb1-O7 ($\times 2$)	2.451(9)	Pb2-O4	3.098(11)
		Pb1-O8 ($\times 2$)	3.045(13)	Pb2-O4	2.8879(5)
				Pb2-O5	2.723(12)
				Pb2-O6	2.603(13)
				Pb2-O8	2.825(13)
<Pb-O>	2.868	<Pb1-O>	2.866(3)	<Pb2-O>	2.761(3)
Re-O ($\times 6$)	1.962(3)	Re1-O1 ($\times 2$)	1.942(4)	Re2-O2	1.981(11)
		Re1-O6 ($\times 2$)	1.981(11)	Re2-O3	2.024(19)
		Re1-O7 ($\times 2$)	2.020(19)	Re2-O4 ($\times 2$)	1.943(4)
				Re2-O5	1.960(11)
				Re2-O8	1.970(23)
<Re-O>	1.962	<Re1-O>	1.981(5)	<Re2-O>	1.970(6)
Mn-O ($\times 6$)	2.093(3)	Mn1-O1 ($\times 2$)	2.076(4)	Mn2-O2	2.019(11)
		Mn1-O5 ($\times 2$)	2.099(11)	Mn2-O3	2.222(18)
		Mn1-O8 ($\times 2$)	2.105(22)	Mn2-O4 ($\times 2$)	2.084(4)
				Mn2-O5	2.200(11)
				Mn2-O8	2.106(18)
<Mn-O>	2.093	<Mn1-O>	2.093(6)	<Mn2-O>	2.119(5)

Table 3. Selected refined bond distances ($\text{\AA}$) for $\text{Pb}_2\text{MnReO}_6$.

Space group	Lattice vectors	Origin
$C2/m$ (No. 12)	$(-1/2, -1/2, 0), (0, 0, 1), (-1, 2, 0)$	$(0, 0, 0)$
$P2/c$ (No. 13)	$(-1/2, -1/2, 0), (0, 0, 1), (-1, 2, 0)$	$(0, 0, 0)$
$P2_1/c$ (No. 14)	$(-1/2, -1/2, 0), (0, 0, 1), (-1, 2, 0)$	$(0, 0, 0)$
Refined global amplitudes of representations		
Γ_1^+	0.113(19)	
Γ_4^+	0.94(5)	
Γ_5^+	0.43(4)	
Σ_1	0.107(5)	
Σ_2	0.68(3)	

Table 4. Space group, lattice vectors and origin respect to the parent cell (high temperature phase). The cells retained have $2/m$ point group and Σ_2 is the driving mode to produce the observed superstructure peaks. Refined global amplitudes of irreducible representations in the refinement with the $C2/m$ cell.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.