Structural properties of Pb$_2$MnW$_{1-x}$Re$_x$O$_6$ double perovskites.

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Abstract. Pb$_2$MnW$_{1-x}$Re$_x$O$_6$ samples have been synthesized and their structure has been determined by powder x-ray diffraction. These samples undergo a first order structural phase transition between 413 and 445 K depending on the composition. Above this temperature, the samples are cubic. Below the transition temperature, solid solutions are found for $x \leq 0.2$ and $x \geq 0.5$. The W-rich samples adopt an orthorhombic cell whereas the Re-rich compounds are monoclinic. In the intermediate region, $0.2 < x < 0.5$, both phases coexist. X-ray absorption spectra did not reveal significant changes in the local structure for either Pb, Mn or Re atoms across the structural phase transition. All atoms exhibit distorted environments in the whole series. In the case of Pb and W(Re) atoms, the local distortion remains in the high temperature phase. Samples with $x \leq 0.2$ also show a sharp discontinuity in the dielectric permittivity at the phase transition temperature indicating the presence of a concomitant electrical ordering in the bulk grains. Such an anomaly in the dielectric constant is not observed for the $x \geq 0.5$ samples, compatible with the lack of dipole ordering for this composition range. The different electrical behavior also explains the differences in the entropy content for the two types of transitions.

(Some figures in this article are in colour only in the electronic version)

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1. Introduction.

There is an important interest in the study of materials showing magnetic and electric orderings because they present intriguing physical properties [1] and they are also attractive for technological applications [2-3]. A promising way to obtain materials with both types of orderings is the synthesis of double perovskites combining the presence of stereochemically active cations on the A-site and magnetic cations on the B-site. A double perovskite is described by the formula \( \text{A}_2\text{BB}'\text{O}_6 \) in order to emphasize the long range ordering of B-sites following a rock-salt pattern [4]. Large differences between B and B’ cations in either oxidation state or size favour their ordering. Several members of the double perovskites composed by two cations with partially filled d-shells are ferro- or ferrimagnets and some of them exhibit magnetoresistance effects [5-6]. In addition, the presence of \( \text{Bi}^{3+} \) or \( \text{Pb}^{2+} \) on the A-site favours the appearance of polar structures. This is due to the \( 6s^2 \) lone-pair and the strong covalent character of both Bi-O and Pb-O bonds which stabilize a noncentrosymmetric distorted environment [7-8]. Combination of both types of cations leads to the coexistence of ferromagnetism and ferroelectricity in some materials that can even be grown as thin films [9-10].

It is well known that the physical properties of these compounds are very sensitive to small changes in the chemical composition and disorder can modify either the magnetic ground state or the dielectric response of the material. In a previous study we have found a para-antiferroelectric phase transition in \( \text{Pb}_2\text{MnWO}_6 \) at \( \sim 445 \) K [11]. This transition is coupled to a structural phase transition. At high temperature, \( \text{Pb}_2\text{MnWO}_6 \) is cubic and transforms into an orthorhombic structure with collinear antiferroelectric displacements of \( \text{Pb}^{2+} \) cations below 445 K. These atoms have a distorted first coordination shell in the orthorhombic phase but Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy revealed a similar local disorder around Pb and W atoms for both cubic and orthorhombic phases. Hence, dynamic disordered distortions exist in the cubic phase freezing in an ordered pattern below 445 K and the transition can be classified as an order-disorder type [12]. Afterwards, we have found a similar structural transition in \( \text{Pb}_2\text{MnReO}_6 \). In this case, this compound is cubic above 410 K and monoclinic below such a temperature. However, the comparison between the two structural phase transitions reveals important differences. First of all, the phase transition entropy is very low in the Re-based sample. Secondly, the frozen distortions at low temperature are different for both compounds and in the case of \( \text{Pb}_2\text{MnReO}_6 \), only \( 2/3 \) of the \( \text{Pb}^{2+} \) cations are moved away from the symmetry centre in the monoclinic phase [13]. This compound shows spontaneous magnetization below 100 K in agreement with a ferrimagnetic ordering of Mn and Re cations. Nevertheless, the existence of any kind of electric ordering could not be confirmed experimentally due to the high electron conductivity of the sample.

The present work is devoted to the study of \( \text{Pb}_2\text{MnW}_{1-x}\text{Re}_x\text{O}_6 \) compounds. The purpose of this research is twofold. First of all, we want to verify the existence of solid solution in the whole concentration range and monitor how the change in the W/Re ratio affects the type of Pb displacement and the relationship with the simultaneous presence of electrical dipole ordering in the perovskite B-sublattice. Secondly, we want to characterize the type of structural transition in the Re-based compound and related compositions. In order to achieve our objectives, we have performed a thorough structural study using both x-ray powder diffraction (XRD) and x-ray absorption spectroscopy (XAS) in a wide range of temperatures. The study is completed with measurements of heat capacity and electrical properties.

2. Experimental section.

\( \text{Pb}_2\text{MnW}_{1-x}\text{Re}_x\text{O}_6 \) samples \((0 \leq x \leq 1)\) were prepared by solid state chemistry reaction. Stoichiometric amounts of \( \text{PbO}, \text{MnCO}_3, \text{WO}_3 \) and \( \text{ReO}_3 \) were mixed, ground, pressed into pellets and heated in an \( \text{Ar} \) stream twice with an intermediate grinding. The sintering temperature ranges between 710°C \((x=1)\) and 800°C \((x=0)\) depending on the Re/W ratio. All samples were characterized by XRD using a Rigaku D-Max system. The diffraction peaks agrees with the expected ones for a double perovskite although tiny impurities of pyrochlore (Re-rich samples) or \( \text{PbWO}_4 \) (W-rich samples) were found in some batches. However, impurity concentration was always less than 1% in \( \text{wt} \). The
colour of the pellets ranges between brown (Pb₂MnWO₆) and black (Pb₂MnReO₆). The electrical resistivity at room temperature increases as the Re content decreases.

Step-scanned XRD patterns were measured between 10° and 130° (in steps of 0.03°) at room temperature (RT). We used a graphite monochromator to select the Cu Kα 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 [14].

XAS measurements were carried out on the Spanish CRG BM25A (Pb L₃, Re L₃ and W L₃ edges) and BM29 (Mn K-edge) beamlines at the ESRF (Grenoble, France). The spectra at the Re L₃ and W L₃ edges were recorded at RT whereas spectra at the Pb L₃ and Mn K edges were measured at 40 K. Furthermore, for the x = 1 and x = 0.5 samples measurements at both the Pb L₃ and Re L₃ edges were performed at different temperatures in the range from 300 to 451 K covering the structural phase transition. Spectra of selected references for all edges were also recorded for energy calibration. All data were collected in transmission mode and pellets of the samples were prepared by dilution with either cellulose or boron nitride with the amount of material calculated to optimize the expected signal-to-noise ratio at each absorption edge.

EXAFS spectra, χ(k), were obtained by removing the smooth atomic absorption coefficient using a cubic spline fit. The Fourier transform (FT) of the k-weighted EXAFS spectra has been calculated for the ranges: 1.8 – 9.5 Å⁻¹ at the Pb L₃-edge, 3.0 – 10.0 Å⁻¹ at the Re L₃-edge, and 2.1 – 10.0 Å⁻¹ at the Mn K-edge using a sine window. In the W L₃-edge case, due to interference with the Re L₃-edge (barely ~ 300 eV above), the energy range for the spectra of the Re-doped samples is very short and only a qualitative analysis of the FT obtained for a 2.0 – 7.8 Å⁻¹ range has been carried out. The EXAFS structural analysis was performed using theoretical phases and amplitudes calculated by FEFF-6 code [15] from the crystallographic data of Pb₂MnWO₆ [11] and Pb₂MnReO₆ [13]. We did not account for the Re doping in the theoretical simulations as the W and Re atoms are only one atomic number unit away and thus their scattering properties are very similar. The fits to the experimental data were carried out in R-space with the ARTEMIS programme [16].

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. Electrical measurements were carried out on disc shaped pellets with silver paste electrodes painted onto it. The complex impedance was measured between 1 Hz and 1 MHz with a Solartron 1260 Impedance Analyzer from Schlumberger Instruments. The measurements were performed in air during stepped cooling runs from 510 K down to RT. Before each measurement run, the samples were heated at 520 K for 6 h verifying the absence of changes in their electrical properties.

3. Results and discussion.
3.1. X-ray diffraction.

According to the XRD patterns at room temperature, three different regions can be found in the Pb₂MnW₁₋ₓRxO₆ series depending on the composition. Samples with x≤0.2 show the orthorhombic cell (space group Pnma) of the parent compound, Pb₂MnWO₆ [11]. This unit cell can be derived from the ideal cubic perovskite, Fm-3m, using the lattice vectors (1, 0, -1), (0, 1, 0) and (½, 0, ½). On the other edge, samples with x≥0.5 adopt the monoclinic cell (space group C2/m) of the other parent compound, Pb₂MnReO₆ [13]. The lattice vectors for the monoclinic cell with respect to the cubic one are (1, -2, 0), (0, 0, -1) and (½, ½, 0). Figure 1 shows the relationship between the three kinds of unit cells obtained from the graphics facilities of the ISODISPLACE tool [17]. In both composition ranges, there is a solid solution between W and Re atoms. These samples undergo a structural phase transition on heating and the transition temperature (Tₛ) slightly decreases as the Re content increases. Figure 2 monitors the lattice changes for two representative samples, x=0.2 and x=0.5. The unit cell distortion, either orthorhombic or monoclinic, decreases with increasing
temperature and above ~400-445 K, all samples adopt the cubic cell typical of an undistorted double perovskite (space group, \textit{Fm-3m}).

The main difference between both distorted structures (monoclinic-orthorhombic) concerns to the atomic movement of the Pb\textsuperscript{2+} ions. The monoclinic structure can be derived from the cubic cell by the combination of BO\textsubscript{6} (B=Mn, W or Re) tilts about the monoclinic \textit{y}-direction and the atomic shifts of some atoms. The main displacement is observed in the Pb atoms placed at the \textit{8j} positions in the monoclinic cell [13]. These atoms are shifted by \textasciitilde0.18 Å away from the ideal cubic positions along the monoclinic \textit{z}-direction which corresponds to the [1 1 0] cubic direction. The shift is in opposite directions (+\textit{z} and \textit{−z}) for successive rows of Pb atoms along the long \textit{a}-axis. Each couple of these Pb rows are separated by a third row of Pb atoms located at the \textit{4h} site which remain in the ideal cubic position. Small displacements of B and oxygen atoms lead to distortions in the BO\textsubscript{6} octahedron. Details of this structure can be found in ref. 13. The orthorhombic structure results from large displacements of all Pb\textsuperscript{2+} ions (\textasciitilde0.3 Å) along the [1 0 0] cubic direction. The Pb\textsuperscript{2+} ions approach four oxygen atoms forming a distorted pyramid with them. Atomic shifts are also present for B and O atoms yielding distorted octahedral environments. In this structure, BO\textsubscript{6} tilts have little influence in the global distortion. More details of this structure are reported in ref. 11.

Figure 1. Relationship between the undistorted cubic cell and either the orthorhombic (left) or the monoclinic (right) cells. Big, medium and small balls stand for oxygen atoms, A-cations (Pb) and B(B’)-cations (Mn, W and Re), respectively.

Figure 2. Temperature evolution of the lattice parameters for (a) Pb\textsubscript{2}MnW\textsubscript{0.8}Re\textsubscript{0.2}O\textsubscript{6} and (b) Pb\textsubscript{2}MnW\textsubscript{0.5}Re\textsubscript{0.5}O\textsubscript{6}. The subscripts O, M and C refer to orthorhombic, monoclinic and cubic cells, respectively.
The structural transition is accompanied by an increase in the unit cell volume per formula unit on cooling. However, some differences are observed at $T_S$ between the two types of transition as indicated in the Figure 2. In the transition from the cubic cell to the orthorhombic one, two orthorhombic axes abruptly enlarge ($a$ and $c$) while the $b$-axis is strongly contracted. In the case of $x \geq 0.5$ samples, the monoclinic $c$-axis follows the usual thermal contraction on cooling. Accordingly, the volume expansion is smaller in the cubic$\rightarrow$monoclinic transition than in the cubic$\rightarrow$orthorhombic one [11,13].

![Figure 3. X-ray patterns at room temperature of $x=0.2$ (orthorhombic), 0.4 (mixture) and 0.8 (monoclinic). Inset: Percentage of each phase in the $0.2 \leq x \leq 0.5$ composition range.](image)

At first glance, the diffraction patterns at room temperature of samples with $0.25 \leq x \leq 0.45$ (see the comparison of Fig. 3) show diffraction peaks of both, monoclinic and orthorhombic cells. This was the reason to map in detail this region of the series in steps of $x=0.05$. The Rietveld analysis of these patterns confirms the presence of both phases. The coexistence of both phases might be ascribed either to polymorphism or a lack of solid solution. The quantification obtained from the x-ray refinements is shown in the inset of the figure 3. The weight fraction of each phase varies almost linearly in opposite ways. This result points out to a miscibility gap and these samples would be composed of a bimodal distribution of $x\sim 0.2$ and $x\sim 0.5$ compounds. In this case, this gap should be also present at higher temperatures and the existence of two cubic phases with two lattice parameters should also be noticeable at the high angle region of the XRD patterns. However, our patterns are compatible with a single cubic phase and therefore, polymorphism below the phase transition could be the most suitable option. The competition between the two phases may arise from either structural inhomogeneities or defects. The preparation of the most stable phase for each composition is very difficult because the monoclinic phase is a metastable kinetic form [13] and the synthesis at higher temperatures or for longer time yields the pyrochlore phase. This is the main difficulty to give a definite answer to the presence of two phases in this composition range.

Figure 4 shows the observed changes in the lattice unit as a function of the composition above and below $T_S$. In the high temperature phase, the cubic lattice continuously increases as the Re content decreases. This is in agreement with the tabulated ionic radii showing that $W^{6+}/W^{5+}$ cations are larger than $Re^{6+}/Re^{5+}$ ones [18]. In the low temperature phase (RT), the differences between orthorhombic and monoclinic cells are produced in two of the three axis of the pseudocubic cell, the distortion (or difference between the three pseudocubic egdes) being higher for the orthorhombic phase.
3.2. X-ray absorption measurements.

The EXAFS study on the Pb$_2$MnW$_{1-x}$Re$_x$O$_6$ series comprises two well differentiated parts. First, we have investigated the effect of Re doping in the local structures at fixed temperature below $T_S$. Secondly, the temperature dependence of the Pb and Re local environments for the $x = 1$ and $x = 0.5$ samples is examined in order to gain insights into the structural change at the phase transition.

**Figure 5.** (a) Modulus of the FT of the k-weighted EXAFS data at the Pb L$_3$-edge for $x = 1, 0.8, 0.6, 0.5, 0.4, 0.2$ and $0$ samples measured at $40$ K (uncorrected for phase shift), (b) Comparison of the modulus of the FT of the experimental (closed circles) and best fit (red lines) k-weighted EXAFS data at the Pb L$_3$-edge for samples $x = 1, 0.5, 0.4, 0.2$. (c) Evolution of the three refined average Pb-O distances and (d) the global average Debye-Waller factors along the whole Pb$_2$MnW$_{1-x}$Re$_x$O$_6$ series.
In regards to the effect of Re substitution in the local structures, the main changes are found in the spectra at the Pb L₃-edge. Figure 5(a) shows the modulus of the Fourier transforms (FTs) at the Pb L₃-edge for the Pb₂MnW₁₋ₓReₓO₆ series. The strong peak between 1.0 and 2.4 Å corresponds to the first Pb-O coordination shell and it remains practically alike for all samples. Conversely, in the features located in the 2.4 – 4.0 Å region, significant differences can be observed among samples with x<0.5 and x≥0.5. The two peaks that appear in the FT for samples with x<0.5 seem to converge in a single broad one for x≥0.5. The structural analysis at the Pb L₃-edge was performed up to 4.8 Å by using the orthorhombic structure of Pb₂MnWO₆ [11] for all the samples in order to follow the changes observed at R values larger than 2.4 Å. In the orthorhombic structure the Pb environment is very asymmetric and the interatomic distances were grouped for the refinements. Three distances were used for the first shell (12 O), four for the second shell (4 W and 4 Mn) and two for the third shell (6 Pb). In the fits of the EXAFS spectra the overall amplitude reduction factor S₀² was fixed to 1 and the Debye-Waller factors σ² were correlated with the interatomic distances through the Debye function. The internal potential E₀, the Debye temperature θ₉ and the distances were the only variables in the fits. In figure 5(b) we show the best fits for the samples x = 1, 0.5, 0.4, 0.2 as example. The evolution of the three refined average Pb-O distances and the global average σ² as a function of Re content is shown in figures 5(c) and 5(d), respectively. The obtained Pb-O distances are nearly equal for all samples and their σ² values are almost constant. This indicates that the PbO₁₂ polyhedron does not become more symmetric with Re doping but remains as distorted as in Pb₂MnWO₆. In the second and third coordination shells the distances are strongly overlapped. Within the above described model based on the orthorhombic structure, a shortening in the distances to the farther W and Mn atoms and all the Pb ones is obtained for the samples with x>0.5, in agreement with the changes observed in the FTs. Besides, these changes between samples with x<0.5 and x≥0.5 can be correlated with the structural phase transition found by x-ray diffraction, where the distortion is found to be higher for the orthorhombic phase.

The moduli of the FTs for different samples of the Pb₂MnW₁₋ₓReₓO₆ series at the Mn K, Re L₃ and W L₃ edges is shown in figures 6(a), 6(b) and 6(c), respectively. Changes are less noticeable at these edges. We have focused our attention on the first oxygen coordination shell around these atoms. The associated peak is located around ~ 1.5 Å for all the samples in the spectra at the Mn K, Re L₃, and W L₃ edges.

For the data at both the Mn K and Re L₃ edges, we have performed a structural analysis by using a regular oxygen octahedron with only one Mn(Re)-O distance and the coordination number fixed to six, as a starting structural model. At a second stage, the viability of a more asymmetric octahedron in simulating the crystallographic distortion was also checked and the results obtained with this alternative distorted model are also discussed.

The fits of the EXAFS spectra at the Mn K-edge were performed with the S₀² and E₀ parameters fixed to 0.75 and -2.0 eV respectively, which are the values obtained for the x = 1 sample. The fitting results give a Mn-O distance of 2.15 ± 0.01 Å that is nearly invariable for all the compositional range (0 ≤ x ≤ 1), and values for the Debye-Waller factors σ² of ~ 0.007 ± 0.001 Å² that do not change significantly with x; which is consistent with the behaviour of the first peak observed in figure 6(a). When using a distorted octahedron comprising two sets of Mn-O distances with a common σ² for the fit, the refinement of the x = 1 sample yields the two sets of distances equal to 2.07 ± 0.03 (x 2) and 2.19 ± 0.01 (x 4) Å, respectively, and a σ² value of 0.001 ± 0.002 Å². The weighted average of these two Mn-O distances agrees with the value obtained in the model with a single distance, and the main difference is a σ² about five times smaller. These results indicate that the local structure of the Mn atoms is distorted along the whole series.

For the Re L₃-edge S₀² was fixed to 1 and E₀ to 10.3 eV, value obtained for the reference compound ReO₃. The Re-O distance of 1.94 ± 0.01 Å and σ² of 0.011 ± 0.002 Å² obtained in the refinements are found to be the same for the x = 1, 0.8, 0.5 samples. A more distorted oxygen octahedron with
two sets of Re-O distances was also tested for the x = 1 sample, resulting in refined distances of 2.09 ± 0.04 (x 2) and 1.89 ± 0.01 (x 4) Å and σ² reduced to 0.003 ± 0.003 Å². Therefore, it can be concluded that the ReO₆ octahedron is not completely regular but somewhat distorted up to Re content x = 0.5. This can also be inferred from comparison with the spectra of the ReO₃ and ReO₂ reference samples in figure 6(b). The ReO₃ compound has a cubic crystal structure (space group Pm-3m) [19] and the Re first coordination shell is a regular ReO₆ octahedron with the six oxygen atoms at a distance of 1.874 Å. Accordingly, the first peak in the FT is considerably higher in intensity for ReO₃ than the one of the x = 1, 0.8, 0.5 samples. Indeed, we have obtained a σ² factor of the Re-O distance equal to 0.004 ± 0.002 Å² in the fit for ReO₃ by using a crystallographic single distance, which is about three times lower than the value for our double perovskites in the analogous fit. The first peak of the samples resembles more that of the ReO₂ compound that has a monoclinic structure (space group P42/mnm) [20] with two Re-O distances equal to 1.972 (x 2) and 1.997 (x 4) Å.

Figure 6. Modulus of the FT of the k-weighted EXAFS data at the (a) Mn K-edge (x = 1, 0.6, 0.5, 0.4, 0) measured at 40 K, (b) Re L₃-edge (x = 1, 0.8, 0.5 and also ReO₃, ReO₂) measured at RT, and (c) W L₃-edge (x = 0.8, 0.5, 0.2, 0) measured at RT. All of them uncorrected for phase shift.

At the W L₃-edge, the short available k range (~ 6 Å⁻¹) hinders us from performing a quantitative EXAFS analysis. In any case, from the moduli of the FT it can be said that the WO₆ octahedra seem to become more regular with Re doping since the peak corresponding to the W-O shell increases in intensity. For the pure W double perovskite (x = 0 sample), the local structure of the WO₆ is highly asymmetric with two W-O distances equal to ~ 1.89 ± 0.04 (x 5) and 2.28 ± 0.08 Å as described in [12].

Therefore, the Re doping does not affect the local structure of the MnO₆ octahedra in the Pb₂MnW₁₋ₓReₓO₆ series. However, it induces a change from strongly distorted BO₆ octahedra (B = W, Re) in the W-rich samples to slightly more symmetric ones in the Re-rich samples. This is in agreement with the W(Re)-O distances distribution obtained by x-ray diffraction for the series.

The local structure has also been studied as a function of temperature for the x = 1 and x = 0.5 samples at the Pb L₃ and Re L₃ edges. We show in figure 7 the modulus of the FTs at the Pb L₃-edge for the two samples at different temperature values ranging from 300 to 451 K. For both
samples, the main effect upon heating above room temperature is an overall intensity decrease. The fits of the EXAFS spectra at the Pb L3-edge were carried out as already described in the previous paragraph. The refined Pb-O distances do not vary with temperature, and therefore the local structure around Pb maintains the distortion above Ts (~ 410 and 420 K for x = 1 and x = 0.5 respectively), where the XRD results give an average cubic structure. We have tried to fit the data at 451 K with the cubic crystal structure of Pb2MnReO6 that has a single Pb-O distance equal to 2.868 Å. The latter results in much worse fits with \( \sigma^2 \) of the Pb-O distance about three times larger than those obtained with the distorted model. In the inset of figure 7 the evolution with increasing temperature of the refined Debye-Waller factors by using the distorted model is shown. They exhibit a continuous increase as expected from the moduli of the FT and no anomaly is seen at the phase transition. For the Re L3-edge, no variations with temperature can be appreciated in the FTs for any of the two samples. The same finding was reported at the W L3-edge for the x = 0 sample [12].

**Figure 7.** Modulus of the FT of the k-weighted EXAFS data at the Pb L3-edge measured at different temperatures from 300 to 451 K for samples x = 1 and x = 0.5 (uncorrected for phase shift). Inset: evolution of the average Debye-Waller factors for the Pb-O distances with temperature in the samples x = 1 (black symbols on-line) and x = 0.5 (blue symbols on-line).

3.3. Heat capacity.
The phase transitions have been probed by heat capacity measurements. Figure 8 shows DSC measurements (heating scans) on representative samples. Two types of phase transition can be established from these curves. Samples with x \( \geq 0.5 \) show a rounded endothermic peak in the heat capacity between 413 (x=1) and 419 K (x=0.5). The transition temperature reasonably agrees with the one obtained from XRD. We have measured heating and cooling scans at the speed of 10 K min\(^{-1}\) and a clear shift of ~6 K is observed. This result suggests a first order transition. The calculated phase-transition enthalpy, \( \Delta H = \int \Delta C_p(T) \, dT \), for these samples ranges between 715 and 852 J mol\(^{-1}\) and the total change in the entropy, \( \Delta S \), is between 0.20 \( R \) and 0.24 \( R \), \( R \) being the gas constant. This can be considered the entropy change in the transition from the monoclinic phase to the cubic one.

Heat capacity reveals stronger peaks for samples with x \( \leq 0.2 \). The transition temperature is around 448 K and a similar temperature shift is observed between heating and cooling scans. The estimated phase-transition enthalpy is higher for these samples and it ranges between 2615 and 2690 J mol\(^{-1}\). This yields a total change in the entropy between 0.20 \( R \) and 0.24 \( R \), i.e. close to \( R \ln2 \). Therefore, this is the entropy change in the transition between orthorhombic and cubic phases. The reported entropies for similar phase transitions in related double perovskites range between 1.39 \( R \) (i.e. \( R \ln4 \)) [21] and \( \sim 0.3R \) [22]. The large change observed in Pb2MnWO6 and x \( \leq 0.2 \) samples may be ascribed to the ordering process of dipoles due to cooperative displacements of Pb ions [11]. The small value for x \( \geq 0.5 \) samples suggests the presence of significant structural disorder in the low temperature phase as reported for Pb2MgTeO6 [22].
Finally, samples with intermediate composition (0.25 ≤ x ≤ 0.45) show two transitions in the heat capacity as is observed for the x=0.4 sample in the Figure 8. The two peaks are in agreement with the presence of two phases as indicated by XRD patterns. The shape and intensity of both peaks depend on the composition and the two temperatures reasonably agree with the transition from the respective monoclinic and orthorhombic phases.

3.4. Electrical properties.
The electrical properties of Pb$_2$MnWO$_6$ and Pb$_2$MnReO$_6$ samples have been already reported [11,13]. Here, we complete the study of the series reporting the properties of two selected samples, Pb$_2$MnW$_{0.8}$Re$_{0.2}$O$_6$ and Pb$_2$MnW$_{0.4}$Re$_{0.6}$O$_6$. The total electrical resistance of the samples was obtained from the low frequency intercept of the Nyquist plot (Z$_{im}$ vs. Z$_{re}$) with the Z$_{re}$ axis. Nyquist plots of both compounds at around 75 °C are given in Fig. 9, scaled to the sample dimensions for better comparison. The lines are fits to the experimental data, using the models described below. The conductivity is due to electronic carriers (electrons or holes), as there is not relevant polarization associated to charge transfer with the metallic electrodes. The conductivity obtained from these measurements is plotted in Fig. 10 as a function of inverse temperature, together with the conductivity of Pb$_2$MnWO$_6$ and Pb$_2$MnReO$_6$ taken from ref. 11 and 13. Clearly, the electrical conductivity increases as the W content in the sample decreases. Moreover, the activation energy ($E_a$) decreases with increasing the Re content. Both facts may be related to the increase of electron density in the 5$d$ bands induced by the substitution of W with Re. Pb$_2$MnReO$_6$ is semiconductor showing a small change in the $E_a$ at $T_s$ [13]. A similar result is now found for Pb$_2$MnW$_{0.4}$Re$_{0.6}$O$_6$ where a slight slope change in the conductivity is observed around the temperature of the structural phase transition.

In Fig. 9 one can clearly observe differences between both samples. The Nyquist diagram of Pb$_2$MnW$_{0.4}$Re$_{0.6}$O$_6$ shows a single arc in all the measured temperature range and the data have been analyzed using a single RQ element (resistance in parallel with a constant phase element) [23]. The frequency of maximum loss moves from 5 KHz to 1.2 MHz as temperature increases from 50 ºC to 240 ºC, as correspond to the increase in conductivity. The equivalent capacitance for this sample is almost constant in the experimental temperature range and takes values between 5 and 5.7 nF. That is, the ratio between the effective sample capacitance and the capacitance of the empty cell ($C_0$) stays around 9000 (see Fig. 11). These capacitance values, as well as they being temperature independent, are typical of polarization at dielectric grain boundaries [24] in ceramics with several microns sized grains. Within this model, the bulk contribution to the impedance should be at higher frequencies, out of our experimental setup. The bulk conductivity has to be high enough to be compatible to the observations. In fact, the total resistance is dominated by this grain boundary.
contribution. Alternatively, in the event of very high dielectric constant of the bulk material, both contributions (grain and grain boundary) could have almost equal relaxation times. Then, the process with the largest resistance would dominate the impedance spectra, the other process remaining masked. If this were the case, again the grain boundary contribution appears to dominate the experiment taking into account the temperature dependence, and the relative permittivity of the grain interior should have to be larger than $10^4$ at all temperatures, a very high value not easy to explain. Consequently, we have no information on the dielectric constant of the grains (the bulk material) in this sample, whose relaxation lies most probably at frequencies larger than the ones available in our equipment.

**Figure 9.** Nyquist plots of electric resistivity measured for Pb$_2$MnW$_{0.4}$Re$_{0.6}$O$_6$ (top) and Pb$_2$MnW$_{0.8}$Re$_{0.2}$O$_6$ (bottom). The lines are fits using the models described in the text.

**Figure 10.** Conductivity vs $1000/T$ for the indicated samples. The straight lines are fits to the Arrhenius equation. Activation energies are indicated for each fit.
The Nyquist plot of $\text{Pb}_2\text{MnW}_{0.8}\text{Re}_{0.2}\text{O}_6$ shows two arcs partly overlapped. The experimental data were fitted with two (RQ) elements in series, and from there, the effective capacitance of each contribution has been determined. The fit yields values around 1.5 nF for the equivalent capacitances of the high frequency (HF) arc and 7 nF for the low frequency (LF) one. The effective capacitance normalized to the empty cell capacitance is plotted in Fig. 11.

The capacitance obtained in the LF arc remains practically constant in the experimental temperature range while the HF contribution shows a clear temperature evolution (see Fig. 11). This capacitance has a maximum at around the structural phase transition. Above $T_S$, it follows a Curie-Weiss law whereas below $T_S$, it remains almost constant. These results can be understood assuming we have a ceramic material composed by grains with a paraelectric phase which undergoes a transition to a phase with ordered dipoles at $T_S$ on cooling. The grains, responsible for the HF contribution, would be connected by dielectric boundaries occupying a minor volume of the sample (brick-layer model) [24]. Within this model, one can estimate the dielectric permittivity of both contributions. The bulk dielectric constant is $C_{\text{HF}}/C_0$, $C_0$ being the capacitance of the empty cell (left axis in Fig. 11) while the grain boundary dielectric constant can be estimated as $\varepsilon_{\text{gb}} = (C_{\text{LF}}/C_0) (\delta_{\text{gb}}/\delta_0)$~30 from the value of $(C_{\text{LF}}/C_0)$ (right axis in Fig. 11) if $\delta_{\text{gb}}/\delta_0$~5×10⁻³ ($\delta_{\text{gb}}/\delta_0$ stands for the volume ratio between grain boundary and bulk contributions). $\varepsilon_{\text{gb}}$ is typical of a dielectric oxide phase whereas the bulk shows a high dielectric constant with a transition at around 420 K, characteristic of a paraelectric to dielectrically ordered transition and correlated to the structural transition from cubic to orthorhombic symmetry at $T_S$ [11].

The $\text{Pb}_2\text{MnW}_{1-x}\text{Re}_x\text{O}_6$ series has been synthesized and the crystal structure has been determined for all samples. These compounds adopt the typical cubic phase of a double perovskite at high temperature. The unit cell volume slightly expands as the Re content decreases. This result agrees with the existence of solid solution between W and Re in the whole concentration range. At low temperature, two crystallographic phases are observed below $T_S$. Samples are orthorhombic for $x \leq 0.2$ while they are monoclinic for $x \geq 0.5$. In the $0.25 \leq x \leq 0.45$ range, the two phases coexist with a linear variation of the weight fraction. Defects or inhomogeneities may be the cause for the coexistence of two polymorphs at low temperature but the presence of a miscibility gap cannot be discarded. These results allow us to outline the pseudo-phase diagram for the $\text{Pb}_2\text{MnW}_{1-x}\text{Re}_x\text{O}_6$ series summarized in the figure 12. Pseudo-phase diagram means that monoclinic samples are metastable phases but this diagram is reproducible following the reported synthetic routes.

![Figure 11](image-url) Relative dielectric permittivity for bulk $\text{Pb}_2\text{MnW}_{0.8}\text{Re}_{0.2}\text{O}_6$ (left axis) and normalized effective capacitance for both $\text{Pb}_2\text{MnW}_{0.8}\text{Re}_{0.2}\text{O}_6$ and $\text{Pb}_2\text{MnW}_{0.4}\text{Re}_{0.6}\text{O}_6$ grain boundary contribution (right axis).
The EXAFS analysis reveals that despite the existence of two crystallographic phases at low temperature, the geometrical local structure around the different metal atoms is nearly identical along the whole series. These atoms do not show regular environments as it is manifested by the presence of a large spread of bond lengths with high values of Debye-Waller factors. Regarding the local structure, the differences between the two crystallographic structures are very small justifying the simultaneous existence of both phases in a composition range (see Fig. 12). On warming, there are not significant changes in the local structure indicating that the high symmetric cubic phase shows a similar degree of local distortion. This result reveals that the structural phase transition can be considered as an order-disorder transition for all samples. Dynamic distortions present in the cubic phase are frozen at $T_S$ following two different patterns to yield either orthorhombic or monoclinic cells. The former is preferred for W-rich samples and the latter for Re-rich compounds.

The transition has significant differences depending on the low temperature phase. The orthorhombic samples have an anomaly in the dielectric permittivity at $T_S$ ascribed to the ordering of electric dipoles in the bulk grain. The impedance spectrum can be modelled by a set of paraelectric bulk grains surrounded by dielectric grain boundaries. The bulk grain undergoes a transition to a phase with ordered dipoles at $T_S$. In the monoclinic samples we can not observe this type of anomaly in the dielectric constant. Only one contribution is observed in the impedance spectra suggesting that the electrical properties of these samples are dominated by the grain boundary contribution. A possible explanation could be the presence of insulating grain boundaries arising from deviations in the oxygen stoichiometry respect to the bulk content [25], with much higher conductivity grain interiors. The bulk contribution in the monoclinic samples might probably be observed at higher frequencies, beyond our experimental setup. All samples show a thermally activated conductivity of electronic type. The activation energy strongly decreases with increasing the Re content.

![Figure 12](image)

Figure 12. Phase diagram of the Pb$_2$MnW$_{1-x}$Re$_x$O$_6$ series. The symbols indicate the experimental points measured by x-ray diffraction. Lines are guide for the eyes.

The different behaviour for both transitions is also observed in the EXAFS analysis, the Debye-Waller factors show an abrupt jump at $T_S$ for W-rich samples [12] while their evolution is
continuous for Re-rich samples. These results suggest that electric ordering is not formed in the monoclinic phase. Accordingly, the heat capacity (and entropy content) is different for each type of structural transition. $\Delta S$ is around three times higher in the orthorhombic→cubic than in the monoclinic→cubic transition. This difference is likely to be due to the simultaneous electrical ordering observed in the former transition [11] and absent (at least not observed) in the latter. This work puts forward the extreme difficulty in the preparation of new multiferroics. The replacement of W by Re permits the preparation of magnetic samples [13] but it is detrimental for the development of electrical ordering.

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**References.**