# Synthesis of new double perovskites $La_{1.98}Mn_{1.11}Mo_{0.89}O_{5.93}$ and $La_{1.92}Mn_{1.29}Mo_{0.71}O_{5.84}$: Characterization of structural and magnetic properties

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## ARTICLE INFO

## ABSTRACT

The synthesis, structural and magnetic characterization of two new perovskites $La_{1.98}Mn_{1.11}Mo_{0.89}O_{5.93}$ and $La_{1.92}Mn_{1.29}Mo_{0.71}O_{5.84}$ are reported. Combined Rietveld refinements of X-ray and neutron powder diffraction data indicate that both samples are monoclinic perovskites with space group $P2_1/n$. The distribution of the transition metals over the octahedral sites is highly ordered: Mn preferentially occupies $2c$ sites, while Mo mostly occupies $2d$ sites. Mn oxidation states were determined by means of high resolution Kβ Emission Spectroscopy. The susceptibility as a function of temperature measurements and hysteresis loops show complex magnetic behaviour of both perovskites. The refined magnetic cells indicate that $La_{1.98}Mn_{1.11}Mo_{0.89}O_{5.93}$ is ferrimagnetic as a result of the antiferromagnetic coupling of two ferromagnetic sub-lattices associated to $2d$ and $2c$ sites, while $La_{1.92}Mn_{1.29}Mo_{0.71}O_{5.84}$ is ferromagnetic due to ferromagnetic alignment of the two sub-lattices. The magnetic overall behaviour of the latter perovskite is interpreted in terms of delocalization of magnetic moments arising from ferromagnetic double-exchange interactions between $Mn^{2+}$ and $Mn^{3+}$.

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## 1. Introduction

Double perovskites are intensively studied since the discovery of the colossal magnetoresistant at room temperature $Sr_2FeMoO_6$ [1]. The flexibility to accommodate many different cations in the A, B and B′ sites of the general formula $A_2BB'O_6$ gives a large versatility for the synthesis of new compounds with properties that can be tailored adequately. Particularly, the proper combination of B and B′ ions can drive many interesting magnetic properties [2–5]. Moreover, the variation in stoichiometry, particularly the relation between B and B′ can change dramatically the magnetic properties [6,7]. It was shown previously that compounds with the stoichiometry $A_3B_2B'O_9$ (where B is a magnetic ion and B′ is a diamagnetic one) have larger $T_C$ values than the corresponding $A_2BB'O_6$ compounds [8]. On the other hand, if B is a magnetic ion and B′ belongs to the second or third transition metals series, because of the large delocalization of the 4d and 5d electrons, half metallic compounds, usually with magnetoresistant properties at room temperature are obtained [9]. The itinerant nature of $Mo^{4+}$ and $Mo^{5+}$ electrons and their distribution among 3d and 4d orbitals was confirmed by Chmaissem et al. [10].

We have studied the $Mn^{2+}$ containing double perovskite $BaLaMnSbO_6$ [5] and found interesting magnetic properties. This compound displays signs of superparamagnetism in the 40–160 K range, which arises from unbalanced antiferromagnetism inside nanoclusters formed by regions which are rich in $Mn^{2+}-O^{2-}-Mn^{2+}$ paths. The possibility of Zener double exchange

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for the similar compound SrLaMnSbO6 has been reported by Greenblath and co-workers [11].

Recently, ordered Mo double perovskites $Sr_2Mg_{1-x}Mn_xMoO_{6-\delta}$ and $Sr_2MgMoO_{6-\delta}$ have been characterized as promising materials for Solid Oxide Fuel Cells (SOFCs) [12,13]. Mo, a 4d transition metal which can be tetravalent ($4d^2$, $t_{2g}^2$, S = 1), pentavalent ($4d^1$, $t_{2g}^1$, S = 1/2) or hexavalent ($4d^0$, $t_{2g}^0$, S = 0), can be adapted to any other B' cation by just regulating the synthesis conditions (oxidizing or reducing atmospheres).

Based on these facts, we synthesize two new double perovskites with general compositions $La_{2-z}Mn_{1+x}M_{1-x}O_{6-\delta}$, particularly $La_{1.98}Mn_{1.11}Mo_{0.89}O_{5.93}$ and $La_{1.92}Mn_{1.29}Mo_{0.71}O_{5.84}$. We make their structural characterization using powder X-ray diffraction (PXRD) and powder neutron diffraction (PND), and magnetic characterization using Magnetization (M) vs. Temperature and M vs. Magnetic field (H) measurements. The oxidation states of Mn were determined by high-resolution X-ray emission spectroscopy (XES) [14].

The objective of this work is to try to find new magnetic materials and to see how changes in composition of the two transition metal cations (the magnetic one ($Mn^{2+}$) and the one that provides the itinerant electrons ($Mo^{4/5+}$)) affect these magnetic properties.

## 2. Materials and methods

Two $La_{2-z}Mn_{1+x}M_{1-x}O_{6-\delta}$ double perovskites were obtained as well-crystallized powders by the standard ceramic method. Stoichiometric amounts of analytical grade $La_2O_3$, MnO and $MoO_2$ (Strem Chemicals) were mixed and ground in agate mortar and pressed into small discs to reduce surface exposure to air. The pellets were placed into an alumina crucible and between two other crucibles with Ti turnings as oxygen getters and heat-treated at 1400 °C for 12 h in Ar atmosphere. The reducing atmosphere was selected in order to stabilize $Mo^{4+/5+}$ oxidation states.

The materials were characterized by PXRD recorded at room temperature (RT) using a PANalytical X'Pert Pro diffractometer in Bragg-Brentano reflection geometry operating at 40 kV and 40 mA, with Cu Kα radiation. The scans were performed from 10 to 110°, in 2θ steps of 0.02°, with 8s collecting time. Powder Neutron Diffraction (PND) patterns were collected at D1B and D2B high-resolution lines at Institute Laue Langevin, Grenoble, France. For $La_{1.98}Mn_{1.11}Mo_{0.89}O_{5.93}$ the measurements were performed using λ = 1.287 Å, from 0.1 to 130°, in steps of 0.1°, both at RT and 2K. For $La_{1.92}Mn_{1.29}Mo_{0.71}O_{5.84}$, the diffractograms were collected using λ = 1.59 Å, from 0.1 to 150°, in steps of 0.05°, at RT and 10 K. The structural analysis was done by Rietveld refinement [15] using the Fullprof software [16]. Peak shape was refined with a pseudo-Voigt profile function.

Manganese oxidation state was determined by High-resolution Kβ Emission Spectroscopy [17]. Synthetic standards with known oxidation states were used for comparison purposes with the studied samples. The spectral parameter IAD [18] (integral of the absolute value of the difference between two spectra) was selected for determining the Mn oxidation state, since it uses the whole spectrum information and only requires a simple spectrum preanalysis: area normalization and $K\beta_{1,3}$ line alignment. It is well known that this parameter is very suitable for oxidation state quantification even considering direct calculations and minor experimental data treatment [19].

Magnetic characterization was performed in a Quantum Design Superconducting Quantum Interference Device magnetometer (SQUID). The magnetic susceptibility data were collected from 5 to 300 K, with an applied field of 0.1 T, after cooling in the absence of a magnetic field (ZFC) and after cooling under an applied magnetic field (FC). The isothermal magnetization curves were collected at 5 K with magnetic fields up to 5 T.

## 3. Results

### 3.1. Structural characterization

The formation of both the compounds of interest, $La_{1.98}Mn_{1.11}Mo_{0.89}O_{5.93}$ and $La_{1.92}Mn_{1.29}Mo_{0.71}O_{5.84}$, as majority phases is shown in Figs. 1a and 2a through the corresponding PXRD patterns at RT. $La_{1.98}Mn_{1.11}Mo_{0.89}O_{5.93}$ was accompanied by 4 wt % of $La_3MoO_7$ (space group Cmcm N° 63). $La_{1.92}Mn_{1.29}Mo_{0.71}O_{5.84}$ contained 4 wt % of $La(OH)_3$, with hexagonal structure (space group P $6_3$/m N° 176). From the Rietveld refinement of the RT PND patterns in the monoclinic space group $P2_1/n$, the lattice parameters and the final compositions were obtained. Bazuev et al. [20,21] reported the synthesis of a rhombohedral $LaMn_{2/3}Mo_{1/3}O_3$ perovskite. However, chemically related perovskites such as $Sr_2MnMoO_6$, $Sr_2MnWO_6$ and $Ca_2MnWO_6$ [22,23] have been described as monoclinic with the same space group. Minority phases have also been reported [23].

Phase contents were obtained from conventional multiphase Rietveld refinements of PXRD patterns.

The Goldschmidt tolerance factors t were calculated, according to $t = (r_{La} + r_O)/\sqrt{2}[(r_{Mn} + r_{Mo})/2 + r_O]$, before the synthesis for both the ideal stoichiometry $La_2MnMoO_6$ and $La_2Mn_{4/3}Mo_{2/3}O_6$ perovskites. The $r_{La}$, $r_{Mn}$, $r_{Mo}$, and $r_O$ are the room temperature ionic radii reported by Shannon [24] for the $La^{3+}$ cation (in twelvefold coordination), the $Mn^{2+}$, $Mo^{4+}$ and $Mo^{5+}$ cationic radii (in sixfold coordination), and the oxide anion radius (in twofold coordination). The obtained values were 0.91 for both compositions. When this factor is below unity, the perovskite structure might be of lower symmetry than cubic. Also, this value suggests possible large distortions caused by the cooperative rotation of the $BO_6$ and $B'O_6$ octahedral networks, as will be discussed later.

Parameters obtained from the Rietveld refinements are summarized in Tables 1–3. The reported final compositions result from refining La, Mn, Mo and O occupancies with PND data. It is important to note that the scattering lengths of Mo and Mn are 6.715 and −3.73 fm, the meaning of these scattering lengths are explained by Sears, V. F. [25]. These scattering lengths are different enough to refine occupancies which are correlated, with a high confidence. In Table 1 the corresponding lattice parameters and occupancies are presented. In Table 2 the Wyckoff sites, the atomic positions and the isotropic temperature factors ($B_{iso}$) are informed. Selected bond distances and bond angles are shown in Table 3.

Both compounds are monoclinic double perovskites. The unit cell monoclinic distortion is very small, with β-angles very close to 90° (see Table 1). Besides, the octahedral networks exhibit relatively high tilt angles, 15° average (see Table 3 and Fig. 3). The tilt system for this space group is $a^-b^-c^+$, according to Glazer notation [26]. The octahedral tilt angles (δ) were calculated from (Mn/Mo)$_{2d}$–O–(Mn/Mo)$_{2c}$ bond angles (θ), as (180 − θ)/2. The occupancies below unity of $La^{3+}$ and $O^{2-}$ indicate that there are vacancies in A and O sites within the structure, and define the final composition for both double perovskites.

Stoichiometric amounts of pure oxides were mixed to synthesize the ideal $La_2MnMoO_6$ compound. However, the content of Mn ions is higher than the content of Mo ions in the $La_{1.98}Mn_{1.11}Mo_{0.89}O_{5.93}$ perovskite. Consistently, the excess of Mo is still present in the minor phase $La_3MoO_7$, as illustrated in Fig. 4a. Huang et al. [12,13] mentioned that when there are oxygen vacancies the double perovskite structure remains unchanged if the two octahedral-site cations are stable in less than six-fold oxygen coordination. It is possible that the structure of the ordered octahedral network of $La_{1.98}Mn_{1.11}Mo_{0.89}O_{5.93}$ perovskite is stabilized with a higher proportion of the more stable $Mn^{2+}$ ion, in comparison to $Mo^{4+}/Mo^{5+}$