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Electronic properties in intrinsically disordered double perovskites: $Sr_3MnMo_2O_9$ and $Ba_3MnMo_2O_9$ with Mo^{5+} valence state

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ABSTRACT

$Sr_3MnMo_2O_9$ and $Ba_3MnMo_2O_9$ double perovskites with Mo^{5+} valence states have been prepared in polycrystalline form by thermal treatment, in reducing atmosphere (H_2/N_2 flow), of previously decomposed citrate precursors. These materials have been studied by X-ray and neutron powder diffraction (XRPD, NPD), magnetic and transport measurements. At room temperature, the crystal structure of $Sr_3MnMo_2O_9$ is monoclinic, space group $P2_1/n$, with $a = 5.6564(1)$ Å, $b = 5.6383(1)$ Å, $c = 7.9765(2)$ Å, $\beta = 89.994(7)^{o}$; whereas $Ba_3MnMo_2O_9$ presents a cubic lattice, space group $Fm\overline{3}\,m$, with $a = 8.14900(8)$ Å. These samples present a frustrated magnetic interaction below to 12 and 9 K for $Sr_3MnMo_2O_9$ and $Ba_3MnMo_2O_9$, respectively. Semiconductor behaviour, observed either from d.c. or a.c. measurements, was modelled by a variable-range hopping mechanism. This transport behaviour is in accord with the electronic configurations $Mn^{2+}(3\ d^5)$–$Mo^{5+}(4\ d^1)$ and supports the absence of mixed valence states in both double perovkites.

1. Introduction

Double perovskite oxides with the general formula $A_2B'B''O_6$ have been the object of extensive research because of their rich variety of physical properties. Double perovskites are currently of significant interest for the development of renewable energy technologies such as solid oxide fuel cells, thermoelectric (TE) modules and high-temperature superconductors [1–6]. The revival of interest in this family was triggered by a report on Sr_2FeMoO_6 [7], demonstrating that in the electronic structure only minority spins are present at the Fermi level; this material was shown to exhibit intrinsic tunneling-type magnetoresistance (TMR) at room temperature (RT) [7,8].

Despite the large number of double perovskites informed up to now, few studies are devoted to compounds with stoichiometry $A_3B'_2B''O_9$. This particular type of stoichiometry is apparently more complex, but these oxides are also double perovskites $A_2B'_{1.33}B''_{0.66}O_6$ whose crystallographic formula can be re-written as $A_2[B']_a[B'_{1/3}B''_{2/3}]_bO_6$, where *a* and *b* denote the crystallographic sites in the corresponding space group. Thus, they, display an intrinsic partial disordering over half of the perovskite ($B'_{1/3}B''_{2/3}$) positions. Furthermore, this composition offers the possibility of changing the oxidation states of the B′ and B″ ions and consequently modifying the electrical and magnetic properties. Some double perovskites have been reported as ferrimagnets with Curie temperatures (T_C), in some cases, above RT. Previously we have prepared and studied the magnetic properties of some double perovskites with B′ = Fe, as $Sr_3Fe_2MoO_9$, $Ca_3Fe_2WO_9$, $Sr_3Fe_2UO_9$ and $Sr_3Fe_2TeO_9$ and observed a ferrimagnetic behaviour below $T_C = 280$ K, $T_C = 310$, $T_C = 330$ K and $T_C = 717$ K, respectively [9–12]. Also, we have induced a semi-metallic behaviour and colossal magnetoresistance (CMR) properties in these compounds, as that

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recently reported in $Sr_3Fe_2MoO_9$ via chemical reduction, by topotactical removal of oxygen atoms [13]. In addition, the manganese in this structure led to an interesting charge ordering behaviour, as was reported in $Ca_3Mn_2NbO_9$ [14].

In contrast with the $A_3B'_2B''O_9$ family (with A: earth alkaline cations; B': firsts transition metal row; B'': second and third transition row or p-block element) we can also define the related $A_3B'B''_2O_9$ stoichiometry (or $A_2B'_{0.66}B''_{1.33}O_6$; also intrinsically disordered), which makes it possible to tune different oxidation states for B′ and B''. Recently, we have prepared and studied the magnetic and transport properties of $Ba_3FeMo_2O_9$ where the coexistence of localized and itinerant electrons (Fe^{3+}-$Mo^{4+/5+}$) leads to a non-negligible magnetoresistance properties [15]. These results motivated the interest to obtain and study this system but with Mn cations.

In the present work, we describe the results of fully replacing Fe by Mn in the precedent systems, Mn ions being able to adopt varied oxidation states. We report on the synthesis of $Sr_3MnMo_2O_9$ and $Ba_3MnMo_2O_9$ (hereafter labelled SMM and BMM, respectively) double perovskites obtained by precursor method in reduced conditions (H_2/N_2). The well-crystallized samples were characterized by X-ray and neutron powder diffractions and their crystallographic features structure was refined by the Rietveld method. In order to obtain a better understanding of this new system with Mn/Mo = 0.5 we performed magnetic, d.c. and a.c. electrical transport measurements. Finally, the Mn oxidation state was confirmed by X ray absorption spectroscopy experiments.

2. Experimental

SMM and BMM double perovskites were prepared as black polycrystalline powders from citrate precursors obtained by soft chemistry procedures in controlled atmosphere. Stoichiometric amounts of analytical grade $Sr(NO_3)_2$ (or $Ba(NO_3)_2$), $MnCO_3$, and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ were dissolved in citric acid. The citrate and nitrate solutions were slowly concentrated, leading to organic resins containing a random distribution of the cations involved at an atomic level. These resins were first dried at 180 °C and then all the organic materials and nitrates were eliminated in a subsequent treatment at 600 °C in air, for 12 h, giving rise to highly reactive precursor materials.

The conditions for the SMM and BMM synthesis were established from several trials under different conditions of temperature and time, in H_2/N_2 (5/95) atmosphere. The optimal conditions resulted from the treatment in H_2/N_2 (5/95) atmosphere at 1200 °C for 12 h. The rate of heating and cooling was 5 °C min^{-1}. Thermal treatments longer than 12 h did not produce changes in the obtained samples, suggesting that the new samples reached equilibrium with the atmosphere before this treatment time. The initial identification and characterization of the samples was carried out by X-ray powder diffraction (XRPD).

The crystallographic study was carried out from XRPD patterns collected at RT. The experimental XRPD patterns were obtained on a diffractometer Rigaku D-MAX-IIIC with Cu Kα ($\lambda = 1.5418$ Å) radiation. The data were collected over a range of 10-120° (2θ) with a step of 0.02°; the effective counting time was 5 s per step.

For the structural refinements, neutron powder diffraction (NPD) pattern was collected at RT in the D2B neutron diffractometer, with $\lambda = 1.594$ Å, belonging to *Institute Laue Langevin* (ILL), Grenoble, France. The patterns were refined by the Rietveld method [16] using the *FullProf* refinement program [17]. A pseudo-Voigt function was chosen to generate the line shape of the diffraction peaks. In the final runs, the following parameters were refined: scale factors for the main and impurity phases, background coefficients, zero-point error, unit cell parameters, pseudo-Voigt corrected for asymmetry parameters, positional coordinates, anisotropic thermal factors, and antisite disorder of Mn/Mo and occupancy factors for oxygen atoms.

Thermogravimetric analysis was performed in a Shimadzu TG-50H thermal analyzer apparatus using flowing air at 50 mL/min from 25 °C to 1000 °C, at a heating rate of 5 °C/min. About 18 mg of the sample was used in the experiment.

The magnetic measurements were performed in a commercial superconducting quantum interference device (SQUID-Quantum Design MPMS-5S) magnetometer, with fields up to 50 kOe, in the $2 \leq T \leq 300$ K temperature range.

XANES (X-ray absorption near edge structure) studies were performed for the Mn K-edge. These tests were carried out in the D04B - XAFS1-11681 beamline of the Brazilian Synchrotron Light Laboratory (LNLS, Campinas, Brazil). The Mn K-edge absorption spectra were recorded in transmission mode.

The d.c. electrical transport properties were performed with a Keithley multimeter and d.c. current source equipment by the conventional four probe technique. The a.c. measurements were performed in an Agilent 4294A impedance analyzer. In both cases the experiments were carried out between 80 K and 300 K. For these electrical transport experiments, polycrystalline powder was pressed and sintered in the same conditions of the synthesis. For the resistance and impedance measurements the powders were pressed in bar- and disk-shaped pellets respectively and sintered at the same final temperature used in the synthesis.

3. Results

3.1. Crystallographic structure

The XRPD patterns of SMM and BMM (Fig. 1) are characteristic of perovskite structures, cubic for BMM, and showing the splitting of certain high-angle reflections for SMM, typical of a monoclinic symmetry. Minor amounts of $BaMoO_3$ in BMM were detected from XRPD and NPD data.

The structural refinement was performed from XRPD and NPD data at RT. For BMM, the $Fm\overline{3}\,m$ space group (No. 225), $Z = 4$, was considered, with unit−cell parameter related to a_0 (ideal cubic perovskite, $a_0 \approx 3.9$ Å) as $a = 2a_0$. Ba atoms were located at *8c* (¼,¼,¼) positions and oxygen atoms at *24e* (x,0,0) sites. In this space

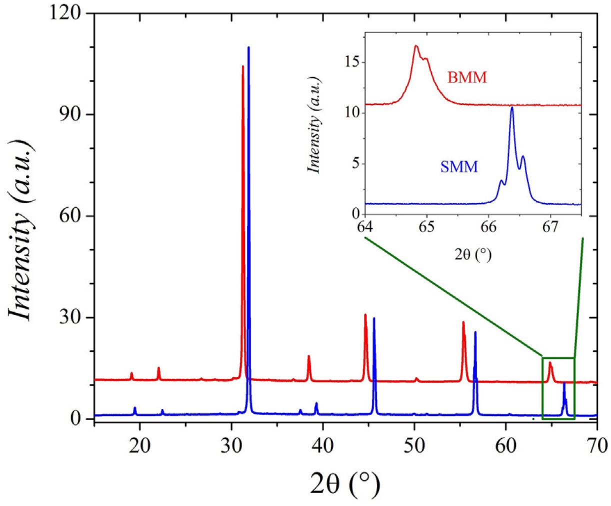

Fig. 1. XRPD patterns with Cu Kα radiation for SMM and BMM. The inset shows the reflections corresponding to the cubic space group $Fm\overline{3}\,m$ for BMM and the splitting typical of a monoclinic distortion for SMM.